

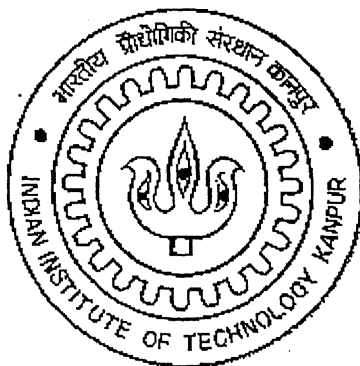
Preparation of Heterogeneous Alumina Catalyst Covalently Binding Mono and Bimetallic Complexes for Alkane Isomerization

*A thesis submitted in partial fulfillment of the
requirements for the degree of*

Master of Technology

By

M. Jhansi Lakshmi Kishore



To the

**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

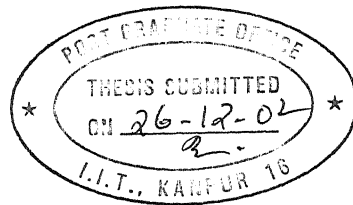
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CERTIFICATE

This is to certify that the work contained in the thesis entitled "**Preparation of Heterogeneous Alumina Catalyst Covalently Binding Mono and Bimetallic Complexes for Alkane Isomerization**", by **Ms. M. J. L. Kishore**, has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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Abstract

In this thesis we have synthesized 2,6-diformyl-4-methylphenol using the procedure given in the literature and prepared the bimetallic complex involving Zr-Zr, Co-Zr, Co-V. We modified the alumina support using phenyl isocyanate and to this, we chemically bound the bimetallic complexes as above. We simultaneously, prepared the monometallic complexes of Zr and compared the isomerization results of n-hexane.

Our experimental results show that monometallic heterogeneous catalyst is more reactive and gives higher conversion compared to the bimetallic catalyst. However the TGA analysis show that the bimetallic catalysts are stable upto 250°C while the monometallic complex is stable upto 209°C.

Chapter 1

INTRODUCTION

In recent years, due to stringent requirements of environmental protection, the design of chemical processes and chemical products is being done by following the principles of green chemistry. This lowers the use and generation of harmful substances in the design and manufacture of chemical products. The use of heterogeneous catalysis improves the yield, selectivity and efficiency and has proven to be a major tool for accomplishing it. The fundamental principles of green chemistry are given below [1].

1. It is better to prevent waste formation than to treat it.
2. To manufacture substances which cause little or no harm to human health
3. The substances used in chemical processes should be such that they cause less accidents, explosions and fires.
4. The processes should be designed such that they are efficient in utilizing all the raw material for producing the final product and also reduce toxicity.
5. The use of solvents, separating agents etc should be minimized.
6. Catalysts should be more useful compared to stoichiometric reagents.
7. Raw materials should be renewable.
8. Avoiding unnecessary derivitazition and modification of functional groups.

In the literature there are several systems (some are given in Table. 1.1) in which use of heterogeneous catalysis has reduced the formation of harmful products [2].

The distillation of petroleum crudes gives petrol, diesel etc. that are linear alkanes. These are mostly burnt and serve as source of fuel. The efficiency of their burning is measured by its octane number and the experiments have shown that branched alkanes burn more efficiently and have higher octane number. Table 1.2[3] gives octane numbers of various hydrocarbons and their branched molecules. As a result of this it is common to isomerize these using $\text{Pt}/\text{Al}_2\text{O}_3$ at about 350-500°C. An effort in this thesis has been made to prepare a catalyst involving a non-noble metal at lower reaction temperatures.

Table: 1.1: Examples of catalysts used to reduce formation of harmful products

Reaction	Catalyst	Principle
Carbonylation reactions	DMC with Zeolites and K_2CO_3	Prevents waste formation, no side products
Alkylation	Palladium catalyst	Efficient use of raw material, less use of solvents and separating agents
Cumene manufacture	Zeolite	Causes less accidents, fires and explosions
Synthesis of poly(Glutamic acid)	Microbial fermentation	Reuse of raw materials
Bleaching in paper and pulp industry	Iron catalyst/ H_2O_2 , POM catalyst	No waste formation, no toxicity
Oxidation of alcohols	Microwave aviation	Reducing the use of solvents and separating agents
Synthesis of 6-amino penicillanic acid	Bio catalysts	Unnecessary modification of functional groups
Synthesis of methyl isocyanate	Catalytic oxidative dehydrogenation	Cause less accidents and explosions

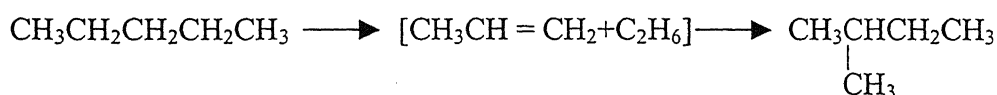
Table: 1.2: Octane numbers of hydrocarbons and their branched molecules

Alkane	Structure	Octane number
n-Butane	C-C-C-C	92
Isobutane	$\begin{array}{c} \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	99
n-Pentane	C-C-C-C-C	61
Isopentane	$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	89
n-Hexane	C-C-C-C-C-C	25
2-Methylpentane	$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	73
2,2-Dimethylbutane	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	96
n-Heptene	C-C-C-C-C-C-C	0
2-Methylhexane	$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	45
2,2-Dimethylpentane	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	93
2,3-Dimethylpentane	$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	96
2,2,3-Trimethylbutane	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	101
n-Octane	C-C-C-C-C-C-C-C	-17

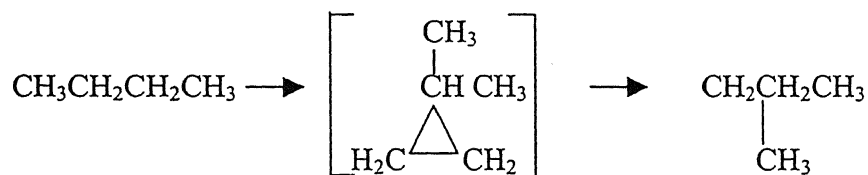
3-Methylheptane	$ \begin{array}{ccccccc} \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & & & & & & & & \\ & & & & \text{C} & & & & & & & & \end{array} $	35
2,3-Dimethylhexane	$ \begin{array}{ccccccc} \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & & & & & & & & \\ & & & & \text{C} & & \text{C} & & & & & & \end{array} $	76
2,2,3-Trimethylpentane	$ \begin{array}{ccccccc} & & & & \text{C} & & & & & & & & \\ & & & & & & & & & & & & \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & & & & & & & & \\ & & & & \text{C} & & \text{C} & & & & & & \end{array} $	102
2,2,3,3-Tetramethylbutane	$ \begin{array}{ccccccc} & & & & \text{C} & & \text{C} & & & & & & \\ & & & & & & & & & & & & \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & & & & & & & & \\ & & & & \text{C} & & \text{C} & & & & & & \end{array} $	103

The mechanism of isomerization of alkanes consists of an overall exchange of alkyl groups and hydrogen. This occurs by the rupture and recombination of pertinent C-H and C-C bonds and involves one of the following step [3].

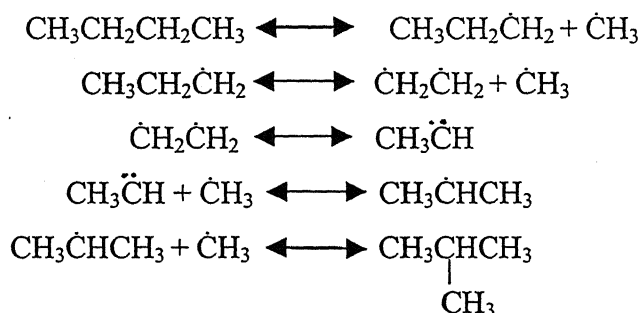
Dealkylation: Dealkylation of the alkane by this procedure forms an alkene and a lower alkane by scission of hydrogen and rupture of a C-C bond, followed by recombination as follows.



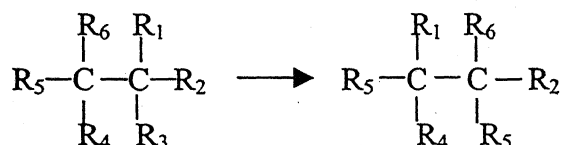
Dehydrogenation and cyclization: By this procedure the alkane first forms intermediate cyclic compound, which further reacts with hydrogen to form an isomer.



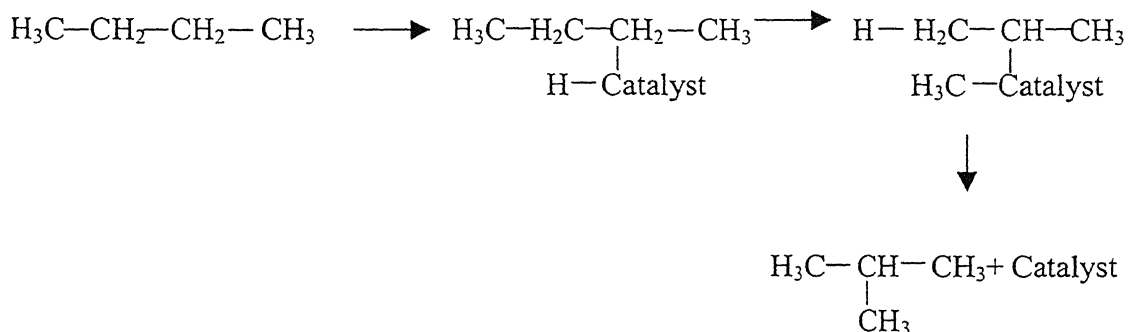
Formation of radicals: The alkanes form alkyl, alkenyl and alkylidene radicals, which are recombined to form new products.



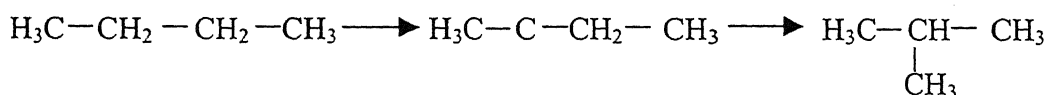
Isomerization without hydrogen shifting: This can be seen in the hexa-alkyl ethanes. The alkyl groups shift instead of hydrogen. The R_1 , R_2 , R_3 , R_4 , R_5 and R_6 below represent the alkyl groups.



Formation of an intermediate compound with catalyst: An intermediate compound is formed between the catalyst and the hydrocarbon and the mechanism can be given as follows.



Thermal isomerization: The molecule first decomposes and then recombines to form an isomer.



In the early days isomerization reactions were carried out at high temperatures (500) without any catalyst. The percent of isomers formed was very low (1-3 %). Later AlCl_3 was used as catalyst and about 25-50 % of isomers were obtained in the temperature range of 400 – 600°C. In the recent years these reactions are being carried out over catalysts with two functions, acid functions (provided by solid acids like Al_2O_3 and zeolites) and metallic function (provided by noble metals, transition metals etc.). The metal salts are loaded on alumina or zeolite supports to form a heterogeneous catalyst. Various methods of heterogenizing the catalyst are given in Table 1.3[4-9].

Zeolites are supposed to be the best materials for preparing isomerization catalysts as they have high number of acid sites and metal can be introduced onto the sites by ion exchange process. Platinum-hydrogen-mordenite catalysts are commercially used for isomerization of C_5 - C_6 , but the stability of these catalysts is found to be low. Yashima et al.[10] studied the effect of time and temperature on the conversion of n-hexane on Pt loaded zeolite catalysts. The conversion showed no change with reaction time (upto 55hrs). The effect of temperature was studied between 400 – 600 K and the conversion was maximum at 548 K. The distribution of products was different for catalysts made of Pt loaded on various zeolites ($\text{H}\beta$, HM and H-ZSM-5). The Pt/ $\text{H}\beta$ showed high conversion (72.4) and selectivity while Pt/HM showed the lowest (14.2). The

Table: 1. 3: Methods of heterozenizing catalysts

Method	Description	Example
Chemisorption of the active component on a support	The metal salts are impregnated on the inorganic support such as, silica or zeolite	<ul style="list-style-type: none"> • Aluminium Chloride on silica which gives high Lewis acidity[5]. • Copper and Zinc nitrates on γ-alumina for methanol reforming[6]
Encapsulation of the active component in the stucture of the catalyst	The metal catalyst is introduced between layers of a clay and the active complex formed hinders its leaching	<ul style="list-style-type: none"> • Graphite intercalated compounds (GICs) of $AlCl_3$, $AlBr_3$, sulphuric acid etc for isomerization reaction [7]. • $MoCl_5$ GIC catalyst for oxidation of propane to acrolein
Physisorption of the active component onto the support	The catalyst consisting of the metal and organic ligand is immobilized through the van der waal type interaction between the functional group of ligand and the surface of the support material.	<ul style="list-style-type: none"> • Immobilization of porcine pancreas lipase on silica microparticles for polymerization of trimethyl carbonate [8]. • Metallocene catalysts supported on silica or alumina for alkene polymerization [9]

products formed were cracking products ($<C_6$), 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane

Tran et al. [11] studied the transformations of butane, n-hexane, and n-heptane over H-mordenite samples with Si/Al ratios of 6.6-8.0 and the reactivity was found to be in the order of n-heptane>n-hexane>butane. The primary products formed are isobutene, propane and pentane in the case of butane, C_3 - C_5 alkanes in the case of n-hexane, C_3 - C_5 alkenes and C_3 - C_6 alkanes in the case of n-heptane. They concluded that the reaction mechanisms are different in benzene, n-hexane and n-heptane. The reaction mechanisms were shown to consist of bimolecular transformations in benzene and monomolecular transformations in the case of n-hexane and n-heptane.

Katrib et al. [12] studied hydroisomerization (i.e., isomerization in presence of hydrogen) of n-hexane with MoO_3 supported on TiO_2 . The catalyst is obtained by impregnating molybdenum in ammonium heptamolybdate salt. The conversion of n-hexane was studied in the temperature range of 500-673 K and it was shown that the conversion increased with temperature. The 2-, 3- methyl pentane isomers were formed with high selectivity. However the selectivity decreased from 90.9% at 600K to 69.5% at 673K. This decrease was attributed to the additional cracking reaction occurring at temperatures higher than 600K. Guevara et al. [13] used sulfate mixed oxide of alumina and zirconia for n-hexane isomerization and the maximum conversion obtained was 18.5%. Pierre et al. [14] studied the alkane isomerizations with catalysts made of molybdenum oxides in the temperature range of 300-450°C. Catalytic cracking and isomerization occurred at temperatures higher than 450°C. At high temperatures catalytic cracking dominates isomerization though it gives high conversion.

Matsushashi et al. [15] studied isomerization of butane in presence of sulfated zirconia and platinum promoted sulfated zirconia at 273-383 K. Isobutane was the main product obtained with a total conversion of 21%. Gallo et al. [16] studied the isomerization of n-heptane in presence of SiC supported MoO_3 -carbon modified catalyst at high pressures up to 40 bar. The main products obtained were dimethyl pentanes. 2-methylhexane, 3-methyl hexane and 3-methyl pentane. Falco et al. [17] studied the effect of platinum concentration on tungsten oxide promoted zirconia on n-hexane isomerization. The catalyst was prepared by impregnation of tungsten oxide-promoted

zirconia up to 1.5% platinum and calcining at 500°C. The catalyst activity and stability was high for platinum concentration of 0.05% and no increase in activity or stability was observed when the platinum concentration was increased.

Arribas et al. [18] studied the bifunctional Pt/WO_x-ZrO₂ (Pt/WZr) heteropolyacid and Pt/ β -zeolite catalysts for hydroisomerization using n-heptane/benzene (25%) feed mixture. The reaction conditions used are 3.0 MPa pressure and temperature range of 200-300°C. For constant n-heptane conversion, the selectivity to isoheptane was the same for both the catalysts, but dibranched and tribranched heptane isomers were higher for Pt/WZr. In the case of benzene, the selectivity to cyclohexane and methylcyclopentane was found to be higher. Boskovic et al. [19] studied the isomerization of n-hexane over catalysts containing 0.5 wt% of Pt on Na (H) Y zeolite. It was found that maximum yield was obtained for catalyst where calcination and Pt-acid decomposition were held simultaneously at higher temperatures. Patrylak et al. [20] studied the isomerization of n-hexane over natural zeolites containing Pd. The conversion varied from 17% to 79.5% in the temperature range of 250-300°C. Chica et al. [21] studied the isomerization of C₅-C₇ alkanes on unidirectional large pore zeolites at 250-300°C. Selectivity and kinetic parameters indicate that differences in pore topology are more important than acidity for determining the isomerization selectivity.

Hua and sommer [22] studied n-heptane isomerization at 200°C over Pt/WO_x/ZrO₂ (Pt/WZ) and alumina doped Pt/WO_x/ZrO₂ (Pt/WZA) catalysts prepared by incipient wetness impregnation technique. The isomers formed were 2-methylhexane, 3-methylhexane, 3-methylhexane, 3-ethylpentane, 2,2-dimethyl pentane, 2,3-dimethyl pentane, 2,4-dimethyl pentane, and 2,2,3-trimethylbutane. Among these 2-methylhexane, 3-methylhexane, are the predominant isomers formed with a selectivity of 36%. The isomerization selectivity was 90% up to 65% conversion and it reduced to 86% at 80 % conversion. Sntamaria et al. [23] studied the catalytic behavior of platinum catalysts supported on Cs beta zeolite/ γ -alumina for n-heptane at 440°C with various concentrations (0-0.85%) of cesium and compared it with a catalyst that has been prepared without zeolite by wetness impregnation of Pt (NH₃)₄(NO₃)₂ in NH₄OH. More cracking products (propane, isobutene and butane) were formed and C₅-C₆ compounds were present in very low concentrations. The only isomerized product obtained was

toluene in the former catalyst whereas in the latter, toluene and isoheptane selectivity was high.

Van Mao and Saberi [24] studied n-heptane isomerization at 225°C over catalysts obtained by the impregnation of Al, Zn and Cd species into a HY-zeolite. All the catalysts enhanced isomerization and reduced cracking. This behavior is ascribed to the formation of desorption-transfer promoting sites, which rapidly remove the carbocationic intermediates from the acid sites preventing any further cracking. The products obtained were C₅-C₇ paraffins. Alvarez et al.[25,26] studied n-heptane transformation on a series of Pt-HY zeolite catalysts containing 0.045 – 0.85 wt % Pt and Si/Al ratio of 9 and 3. The activity per acid site was different for PtHY3 and PtHY9 catalyst. The main products formed were methylcyclohexanes, ethylpentane, dimethylpentane, trimethylbutane, propane and isobutene. Different kinds of zeolites were used in isomerization reactions. The most common zeolite used is mordenite [27-29]. It can be seen that many catalysts are made of metals like Pt, Al, Zn etc supported on zirconia and zeolites are used for isomerization of alkanes.

Objective of the present work:

The catalysts used for isomerization are usually made of noble metals like platinum, ruthenium, rhodium etc., whose metal salts are directly loaded on the support by chemisorption and impregnation techniques. The objective of this thesis is

1. To prepare a catalyst using a non-noble metal metal. An organometallic complex is prepared and chemically bonded to the modified alumina support.
2. To characterize the catalyst for the presence of functional groups, surface area, surface properties and reduction properties.
3. To study the effect of catalyst on isomerization of hexane.

Chapter 2

EXPERIMENTAL DETAILS

The catalyst is prepared by first modifying the alumina by heating at 500°C and then reacting with phenyl isocyanate. The resultant modified alumina is reacted with dichloroethane in presence of Lewis acid catalyst. We have prepared a bimetallic and monometallic complex of the metal that is then covalently bonded to the modified alumina. The detailed steps of the procedure of the catalyst preparation are given as follows.

2.1.Preparation of 2,6–diformyl–4–methylphenol [30] needed for bimetallic complex

2.1.1. NaOH solution is prepared by dissolving 100g of NaOH in 400ml water. 126g (2 moles) of p-cresol is added to this. A golden yellow colored product is developed. Then 37% formaldehyde solution is added. This mixture is stirred and left for 24 hours at ambient temperature (35°C). This mixture is filtered by vacuum filtration and the filtrate obtained is washed with sodium chloride solution 2,6- dimethylol-4-methyl phenol is formed.

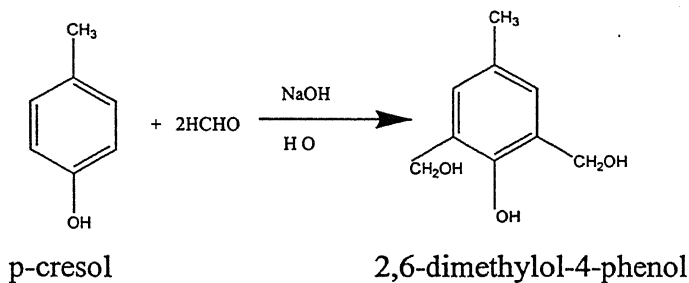


Fig.2.1

2.1.2. The 2,6-dimethylol-4-methyl phenol is taken in a round-bottomed flask provided with stirrer. A 1300ml water and 130ml of 33% NaOH are added to this and stirred. A 494g (2.6moles) of p-toluene sulfonyl chloride dissolved in toluene is added to the above and stirred for 20 hours at room temperature. An aqueous and emulsified phase is formed. This mixture is kept in an ice bath and toluene is added till solids are formed. A white solid tosylated phenol is formed which is separated by vacuum filtration and washed with toluene and dried. 272g of product (Mol. Wt 338) are formed.

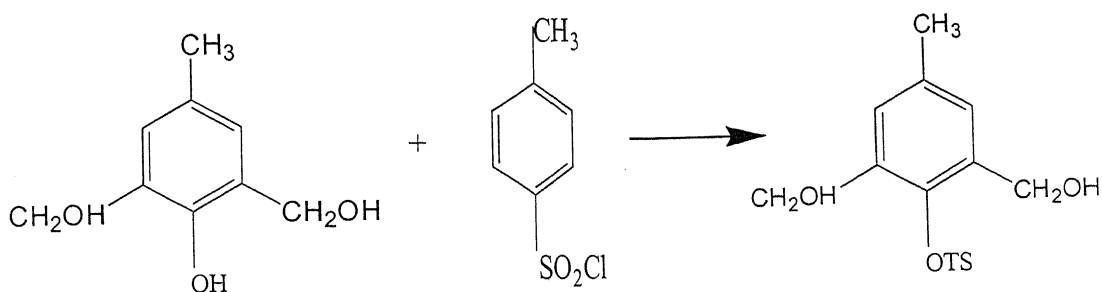


Fig.2.2

2.1.3. The tosylated phenol (272g, 0.8mole) is oxidized with sodium dichromate (208g, 0.69 mole) and acetic acid (645ml). 160ml acetic acid is taken in a 3-necked reactor vessel of 2 litre volume, which is equipped with a stirrer, an addition funnel, and a water-cooled reflux condenser. The sodium dichromate is dissolved in remaining acetic acid (485ml) and introduced through the addition funnel drop wise with stirring for about 40 minutes at 110°C. The reaction mixture is cooled, filtered and washed with water. Green colored crystals of tosylated dialdehyde (250g) are formed.

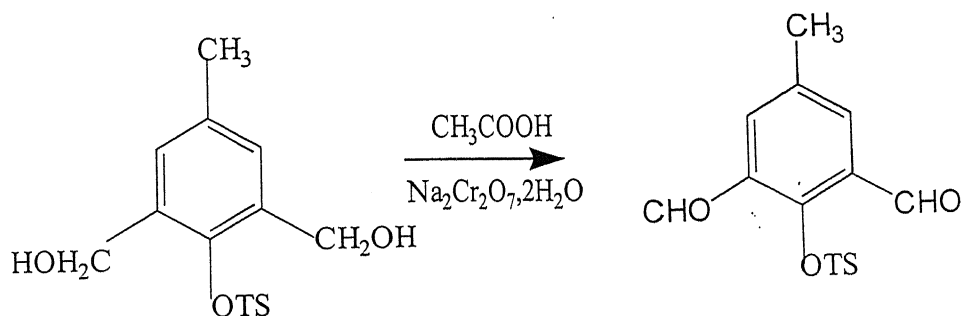


Fig.2.3

2.1.4. Tosylated dialdehyde is taken in a 5-litre beaker and 900ml of H_2SO_4 is added. This is stirred for one hour and ice water slurry is added till the volume becomes 4000ml. The precipitated material is collected by vacuum filtration, washed with water and dried. This is dissolved in toluene and the liquid is recrystallized which yield brownish yellow colored needles. The product obtained is 2,6-diformyl-4-methylphenol. The melting point was determined to be 130°C (133.5°C). The peaks in the $^1\text{H-NMR}$ spectrum that are matched with the literature values are shown in table: 2.1

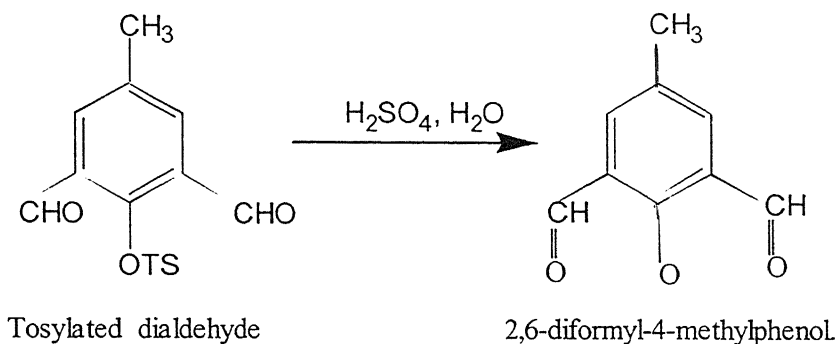


Fig.2.4

2.2. Preparation of bimetallic complex

The bimetallic ligand L^{2-} is a symmetric Schiff base derived by condensing two equivalents of 2,6-diformyl-4-methylphenol with two equivalents of 1,2-phenylenediamine, which gives two identical N_2O_2 sites [31]. The reaction scheme of preparation of complex is shown in fig. 2.5.

2.2.1. Preparation of bimetallic cobalt-vanadium complex:

CoL': To a 50ml N,N-dimethylformamide at 40°C, 2,6-diformyl-4-methylphenol (1.95g, 0.012mol) is added. Then 1,2-phenylenediamine (0.65g, 0.006mol) is added first and cobalt acetate (1.476g, 0.006mol) is dissolved. The solution is stirred until the latter dissolves. After 0.5 hours CoL' crystals precipitate which are washed with diethyl ether and dried. The FTIR spectra of the complex is shown in fig2.6 and it shows C=N (1621cm^{-1}) and C=O (1537cm^{-1}) stretching frequencies.

CoVL': Vanadium sulphate (1.164g, 0.006mol) is added to 20ml of methanol. The CoL' (2.05g, 0.045mol) obtained earlier is added to this and stirred. This is washed with diethyl ether and dried. The FTIR spectra of the complex is shown in fig2.6 and matched for the C=N (1632 cm^{-1}) and C=O (1539 cm^{-1}) frequencies.

CoVL: CoVL' (2g) is added to methanol (30ml). The 1,2-phenylene diamine (0.363g) is added and stirred. The crystals are formed which are washed with diethylether and dried. The FTIR spectra of the complex is shown in fig 2.6 and matched for C=N (1626 cm^{-1}) and C=O (1515 cm^{-1}) frequencies given in the literature. The experimental and analytical values of the C-H-N analysis are given in table: 2.2.

Table: 2.1: The experimental and the literature values of NMR Spectrum peaks

Functional Group	Experimental Value	Reported Value
Phenolic	11.42	11.4
Aldehyde	10.18	10.2
Aromatic	7.74	7.8
Methyl	2.36	2.4

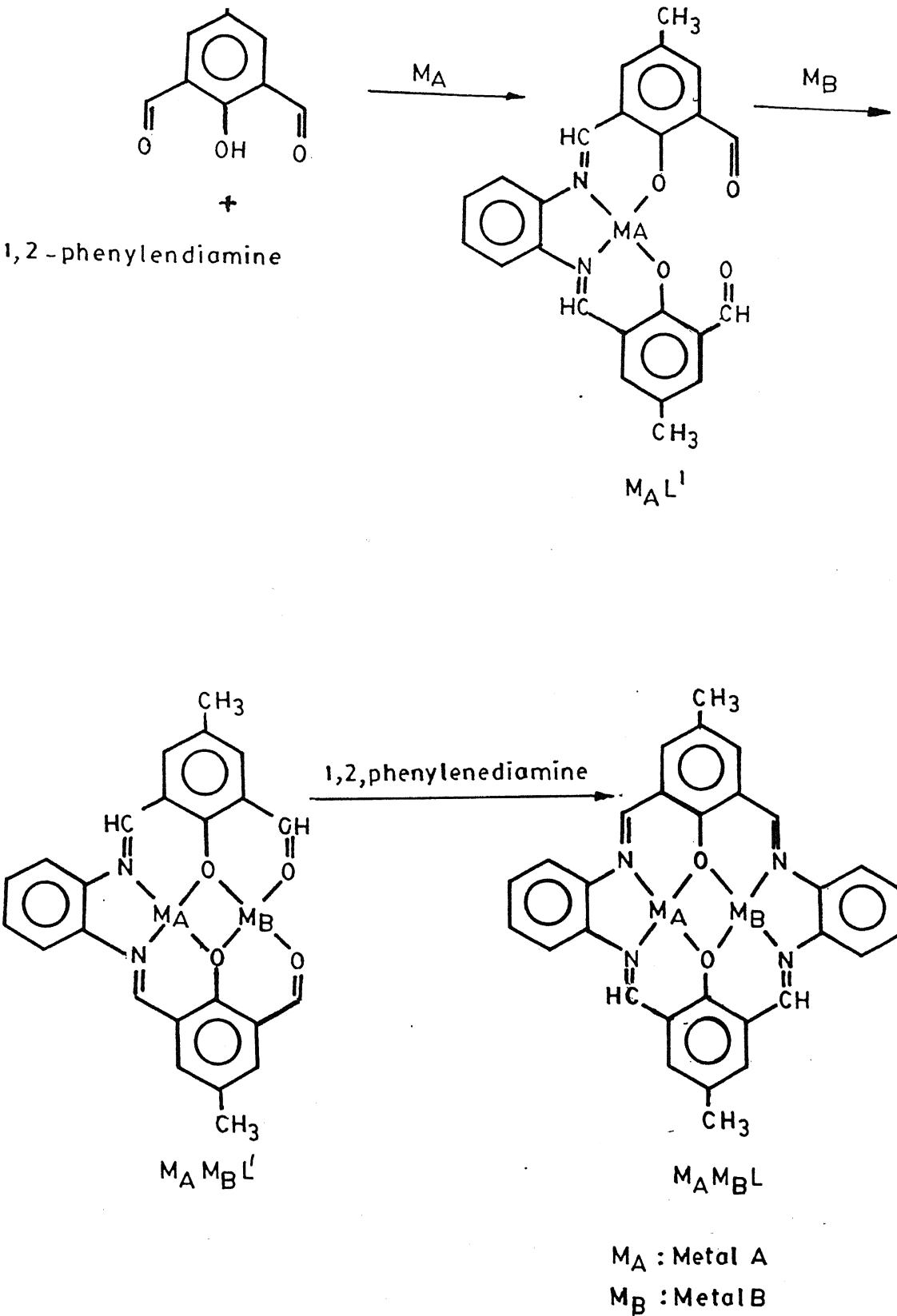
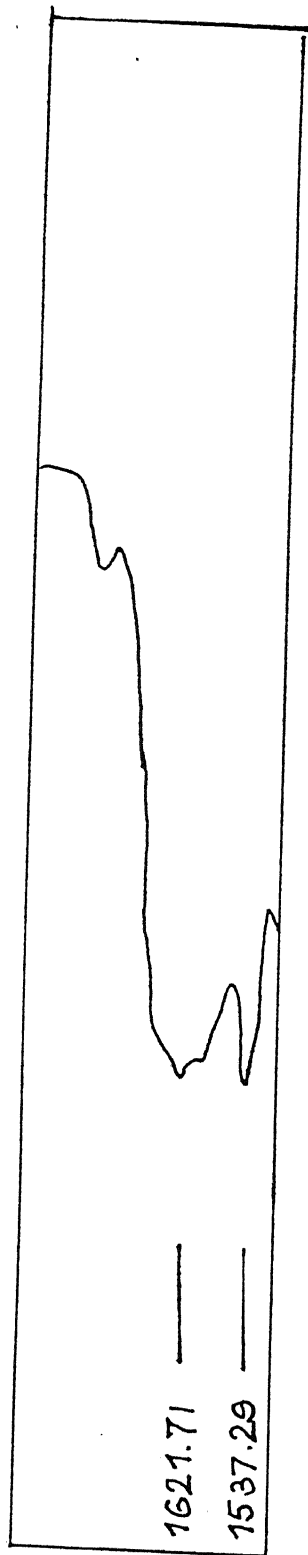
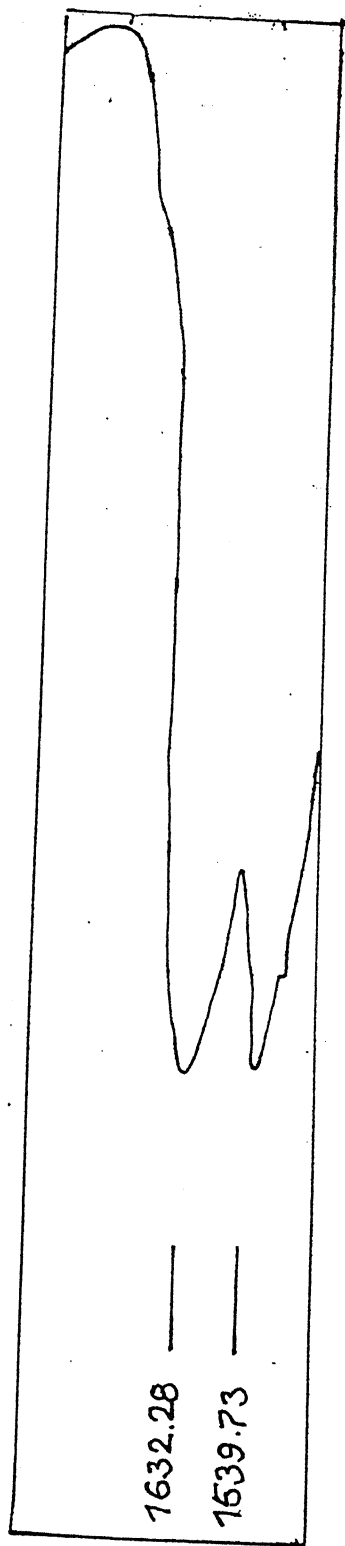


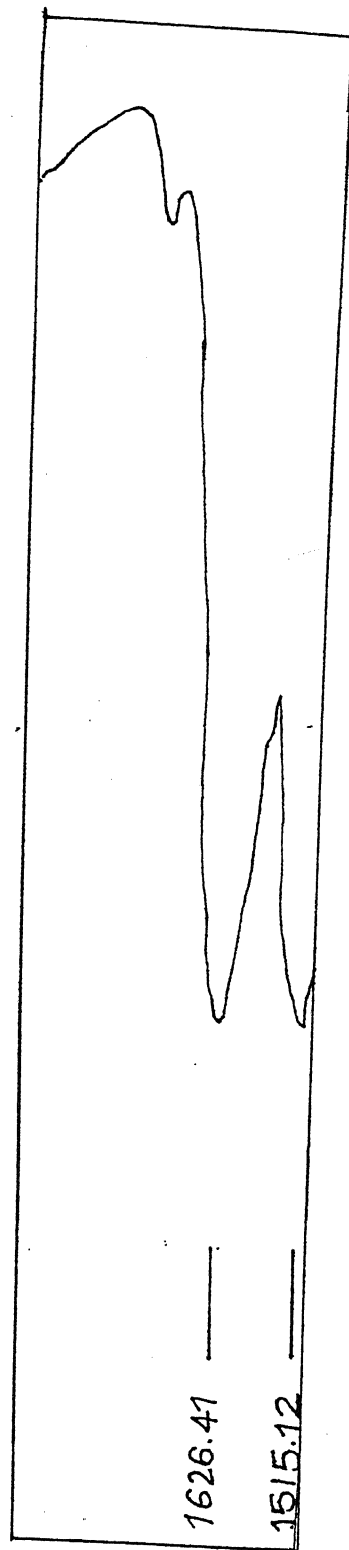
Fig 2.5. Reaction scheme of preparation of bimetallic complex



CoL'



, CoVL'



CoVL

Fig 2.6. FTIR Spectra showing C=N and C=O frequencies of CoL', CoVL', CoVL complexes

2.2.2. Preparation of bimetallic zirconium- zirconium complex

ZrL': N, N-dimethyl formamide at 40°C, 2,6-diformyl-4- methyl phenol (1.95g, 0.012) is added. To this 1,2-phenylenediamine (0.65g, 0.06mol) is added and stirred till dissolved. Then zirconium oxychloride (1.93g, 0.006mol) is added and ZrL' complex is formed which is washed with diethyl ether and dried. The FTIR spectra is shown in fig2.7 and matches for the C=N(1690 cm⁻¹) and C=O (1614 cm⁻¹) frequencies.

ZrZrL': The zirconium oxychloride (2.74g, 0.008mol) is dissolved in methanol (20ml) at ambient temperature and ZrL' (2.74g, 0.005mol) is added. The solution is stirred for 0.5hours and the crystals of the complex are precipitated. This is removed and washed with diethyl ether and dried. The FTIR spectra is shown in fig2.7 and matches for the C=O (1618 cm⁻¹) and C=N (1508 cm⁻¹) frequencies.

ZrZrL: ZrZrL' (2g) is dissolved in 30ml of methanol and 0.336g of 1,2-phenylenediamine (0.336g) is added. The crystals are washed with diethylether and dried. The FTIR spectra is shown in fig2.7 and matches for the C=O (1627 cm⁻¹) and C=N (1512 cm⁻¹) frequencies. The experimental and analytical values of the CHN analysis are given in table: 2.2.

2.2.3. Preparation of bimetallic cobalt- zirconium complex

CoL': To N, N-dimethyl formamide at 40°C, 2,6-diformyl -4- methyl phenol(1.95 is added. Then 1,2- phenylenediamine (0.65g) is added followed by cobalt acetate (1.47g). The solution is stirred until the crystals of cobalt are dissolved. After 0.5hours CoL' crystals are obtained which are washed in diethyl ether and dried. The FTIR spectra of the complex is shown in fig 2.8 and matched for C=N (1670 cm⁻¹) and C=O (1630 cm⁻¹) frequencies given in the literature.

CoZrL': To methanol (20ml) zirconium oxychloride (2.74g) is added at ambient temperature. To this CoL' (2.74g) is added. This is stirred until it becomes homogeneous. washed with diethylether and dried. FTIR spectra of the complex is shown in fig 2.9 and matched for C=N (1624 cm⁻¹) and C=O (1529 cm⁻¹) frequencies given in the literature.

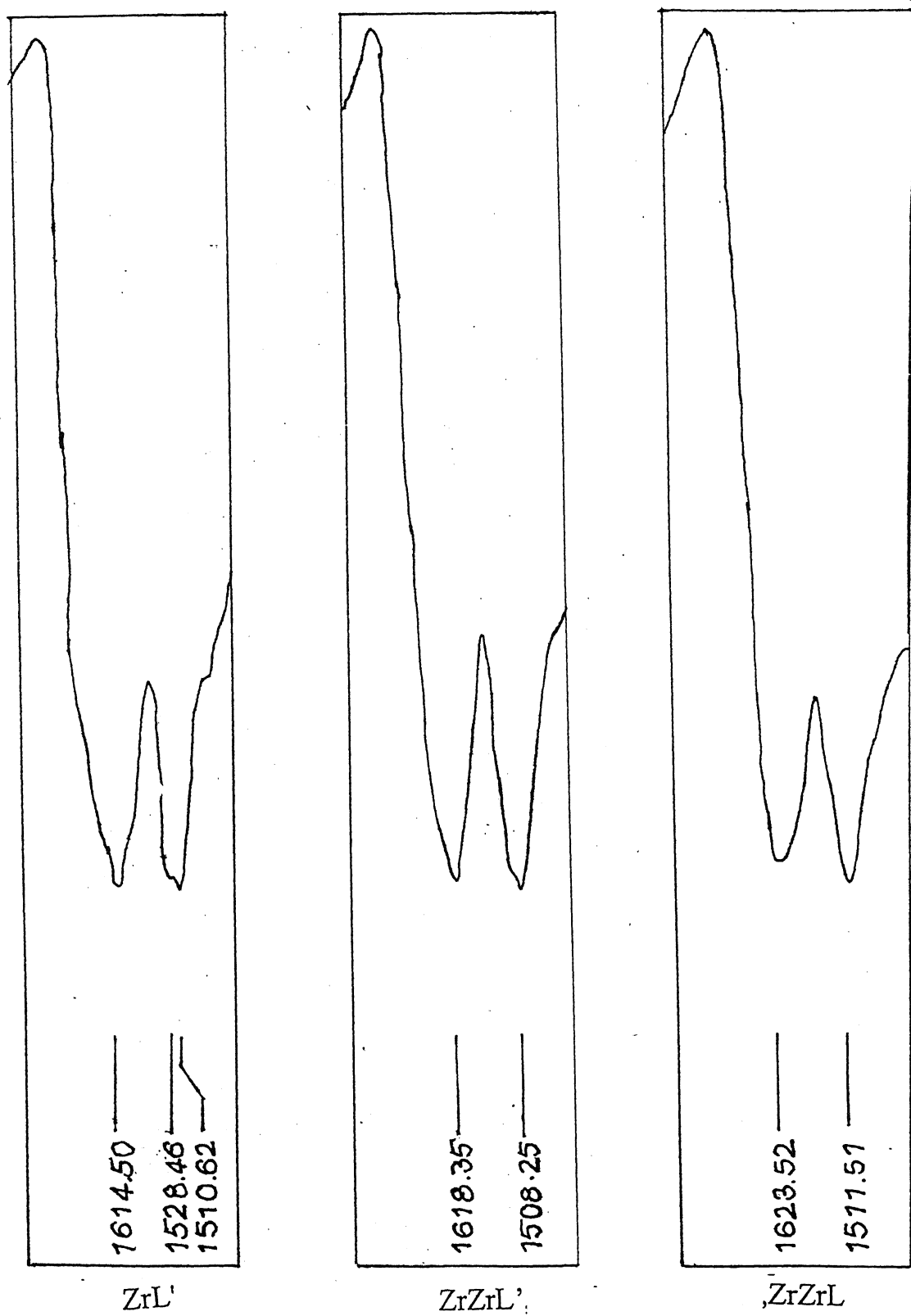


Fig 2.7. FTIR Spectra showing C=N and C=O frequencies of ZrL', ZrZrL', ZrZrL complexes

CoZrL: CoZrL' (2g) is added to methanol (30ml). To this 1,4-phenylenediamine (0.336g) is added and stirred. Crystals are formed which are washed with diethylether and dried. FTIR spectra of the complex is shown in fig 2.10 and matched for C=N and C=O frequencies given in the literature. The experimental and analytical values of the CHN analysis are given in table 2.2.

2.3 Preparation of monometallic zirconium complex:

2.3.1. *Synthesis of complexing agent:*

Salicylaldehyde (24.49, 0.2gmole) is reacted with o-phenylenediamine (10.8g, 0.1mol) by condensation reaction in ethanol (25ml) at the room temperature. The reaction mixture is stirred for 3 hours to get yellow precipitate, which is filtered and dried. The precipitate obtained is 1,2 bis-salicylidene amino-phenylene. The FTIR of the complex is shown in fig.2.9.

2.3.2. *Synthesis of monometallic zirconium complex:*

The bis- (salicylidene amino)-phenylene (1.5g) is added to acetonitrile (100ml) and heated till it is dissolved completely. The zirconium oxychloride (10g) is dissolved in distilled water (200ml) and then mixed with bis- (salicylidene amino)-phenylene solution. The reaction mixture is left for one hour for the precipitation of the monometallic complex. A yellow colored precipitate is formed which is separated by filtration and dried. The precipitate obtained is the zirconium complex.

2.4 Preparation of catalyst:

The alumina after drying at 500°C is found to have a number of hydroxyl groups on its surface and these are schematically shown as below [32].

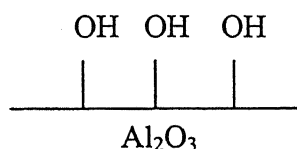


Table: 2.2: Experimental and analytical values of CoVL, ZrZrL, CoZrL

CoVL:

Element	Analytical value	Experimental value
C	62.176	55.363
H	3.79	4.5862
N	9.67	7.229

ZrZrL:

Element	Analytical value	Experimental value
C	55.2	-
H	3.37	-
N	8.58	-

CoZrL:

Element	Analytical value	Experimental value
C	58.15	32.8273
H	3.55	4.8256
N	9.05	8.9979

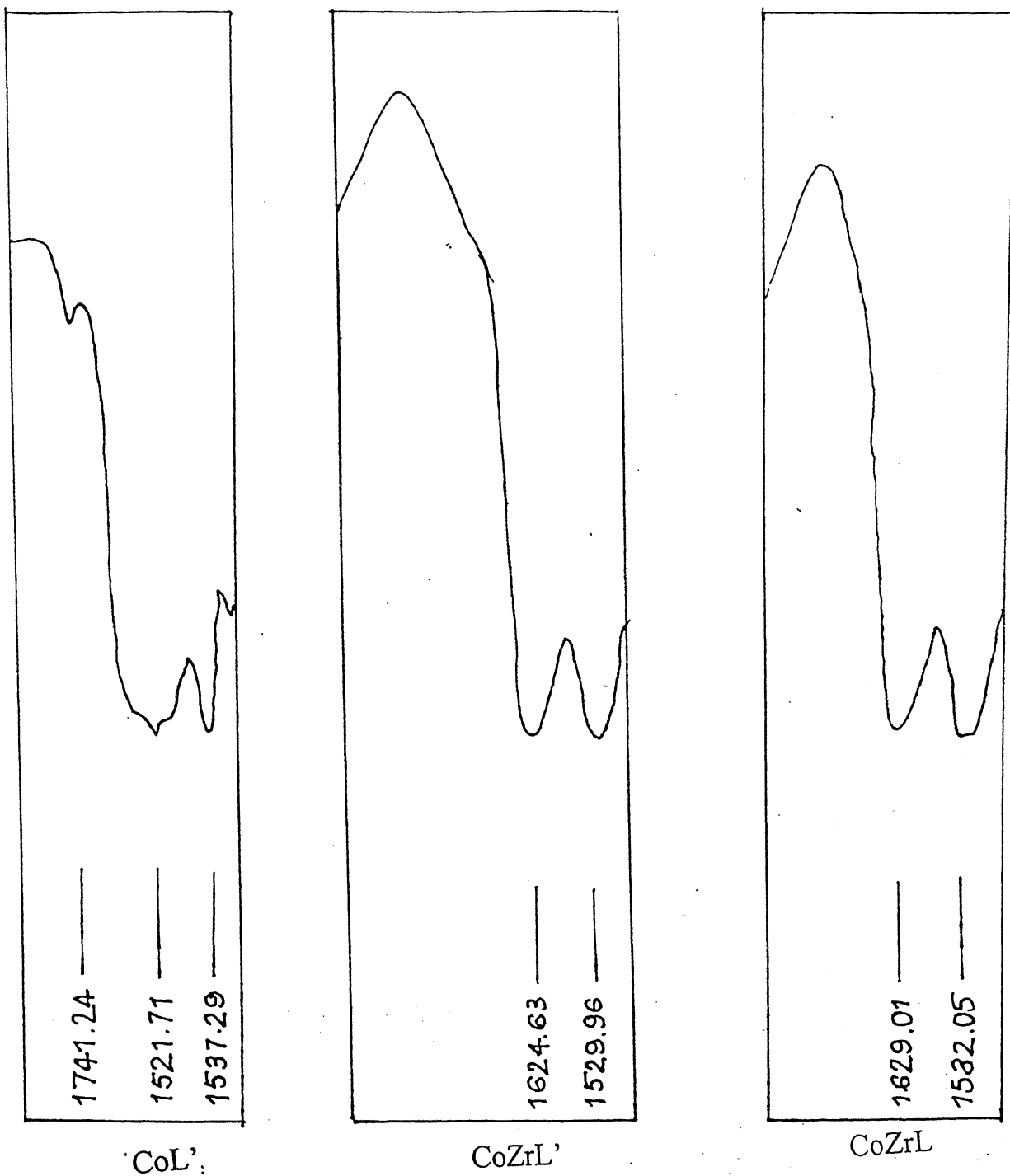


Fig 2.8. FTIR Spectra showing C=N and C=O frequencies of CoL', CoZrL', CoZrL complexes

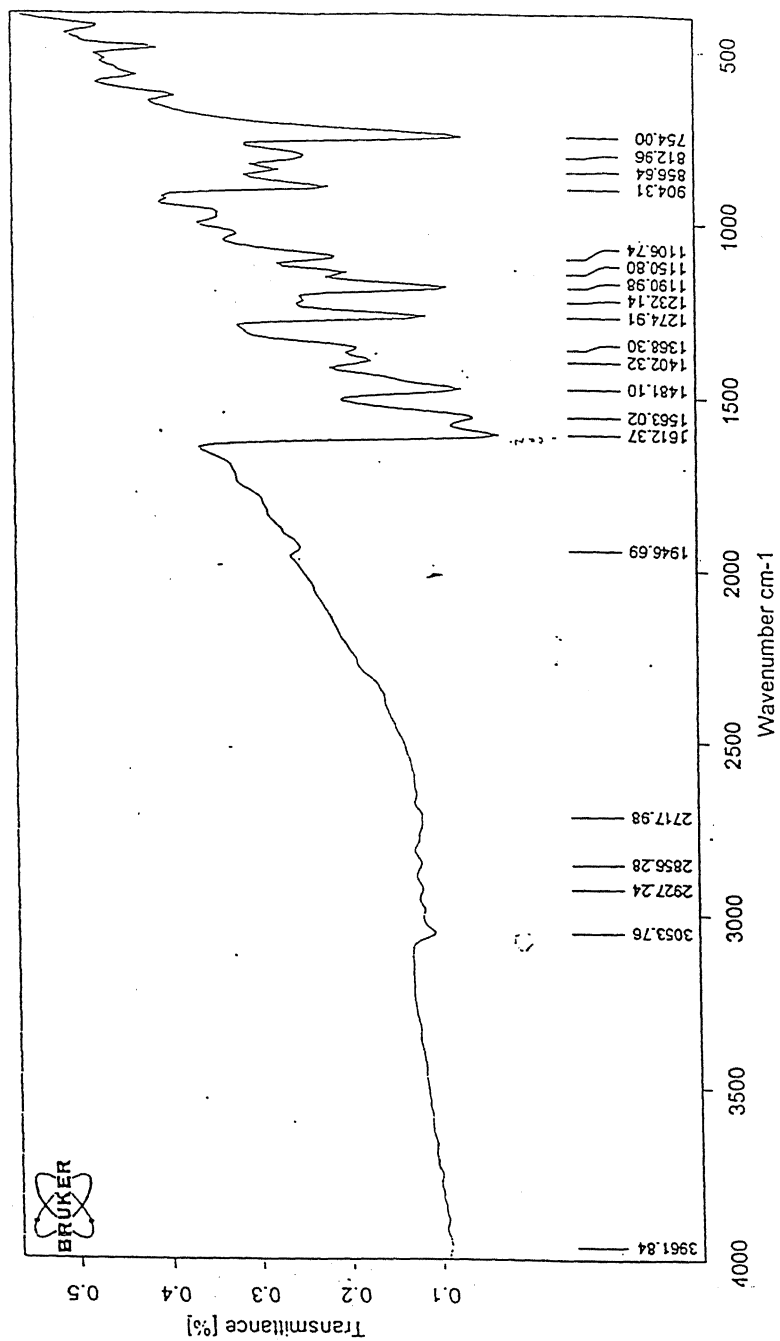


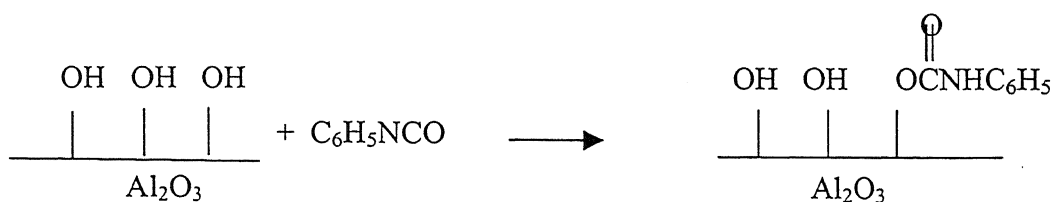
Fig 2.9. FTIR Spectra of 1,2 – bis (salicylaldehyde amino)-phenylene

2.4.1. Modification of alumina

Phenyl isocyanate is prepared by the reaction of sodium azide (35g, 0.4mol) with benzoyl chloride (70 ml) in presence of dry benzene (20ml) at 0° C. Sodium azide is taken in a flat-bottomed flask with dry benzene and kept in an ice bath. Benzoyl chloride is added dropwise with stirring. The reaction is carried out for eight hours. The reaction mixture is vacuum filtered and permeate obtained is collected.



Dried alumina is reacted with phenyl isocyanate for four hours at ambient conditions.



Carbamated alumina (3g) is reacted with 50ml dichloroethane in presence of ZnCl_2 (5 mg) at 80°C for two hours. The product is washed with dichloroethane and dried.

2.4.2. Chemical binding of the metal complex on modified alumina:

The complex is dissolved in methanol and reacted with alumina at 60°C for 4-6 hours. The loaded catalyst is washed and dried which gives the desired catalyst.

2.5. Preparation of dry benzene

Anhydrous calcium chloride is used as moisture absorber to prepare dry benzene. Anhydrous calcium chloride is kept in benzene for 24 hours and then refluxed for 4-5 hours. This reaction mixture is distilled at 75° C to get dry benzene. This is stored over molecular sieves.

2.6. Experimental setup

A high pressure rocking type batch reactor is used for conducting reactions. The reactor is cylindrical in shape made of stainless steel of 400ml volume. The reactor has a provision for gas inlet and pressure gauge. Heating is provided by an external heating coil. Temperature is controlled using an on/off controller with a Cr-Al thermocouple for sensing the temperature.

2.7. Experimental procedure

Isomerization reactions are carried out in a batch reactor with 100ml of reactant and one gram of catalyst. In case of n-hexane, the effect of reaction time (1-8 hours, 100psi initial O₂ & N₂ pressure, 200°C) was studied with Zr/Al₂O₃ catalyst. The effect of reaction time (1-8 hours, 100psi initial O₂ pressure, 200°C) and the effect of temperature (100-200°C, 100psi initial N₂ pressure and residence time of 8hours) was studied with Zr-Zr/Al₂O₃ on hexane.

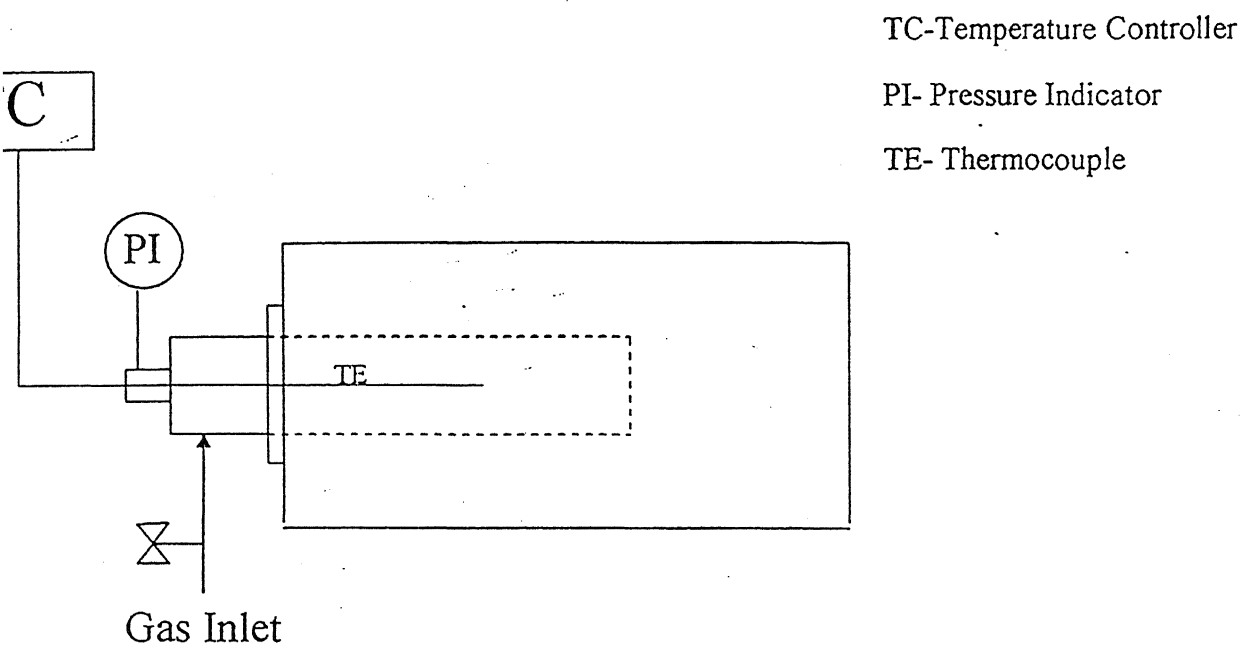


Fig 2.10.Schematic diagram of reaction setup

Chapter 3

CATALYST CHARACTERIZATION

Characterization of a catalyst is important to determine the composition and surface properties. Various methods used for the catalyst characterization are Surface area measurement, Pore size distribution, Infrared spectroscopy, Electron Paramagnetic Resonance (EPR), Mossbaur spectroscopy, X-Ray diffraction, Raman spectroscopy, Temperature Programmed Reduction (TPR) measurement, Scanning Electron Microscopy (SEM). A few of them have been reviewed and given below.

3.1 Fourier Transform Infrared Radiation Spectroscopy

The FTIR spectra of the catalyst at various stages of preparation are analyzed. The FTIR of dried alumina show the presence of -OH groups at a frequency of 3442 cm^{-1} (lit. 3450 cm^{-1}) is shown in Fig.3.1. The FTIR of the phenyl isocyanate synthesized in 2.4.1 is shown in Fig.3.2 and is matched for -CH at 3038 cm^{-1} (lit. 3030 cm^{-1}) and N=C=O at 2258 cm^{-1} (lit. 2358 cm^{-1}). The FTIR of carbamated alumina is shown in Fig.3.3 and matched for -NH groups at 3337 cm^{-1} and -CO at 1650 cm^{-1} . The FTIR of carbamated alumina reacted with dichloroethane is shown in fig.3.4 and matched for N=C=O at 2341 cm^{-1} and C-Cl at 694 cm^{-1} . The FTIR of the final catalyst loaded with monometallic zirconium complex ($\text{Zr}/\text{Al}_2\text{O}_3$) is shown in fig 3.5 and it matches for N-C=O at 2371 cm^{-1} and -OH at 3417 cm^{-1} .

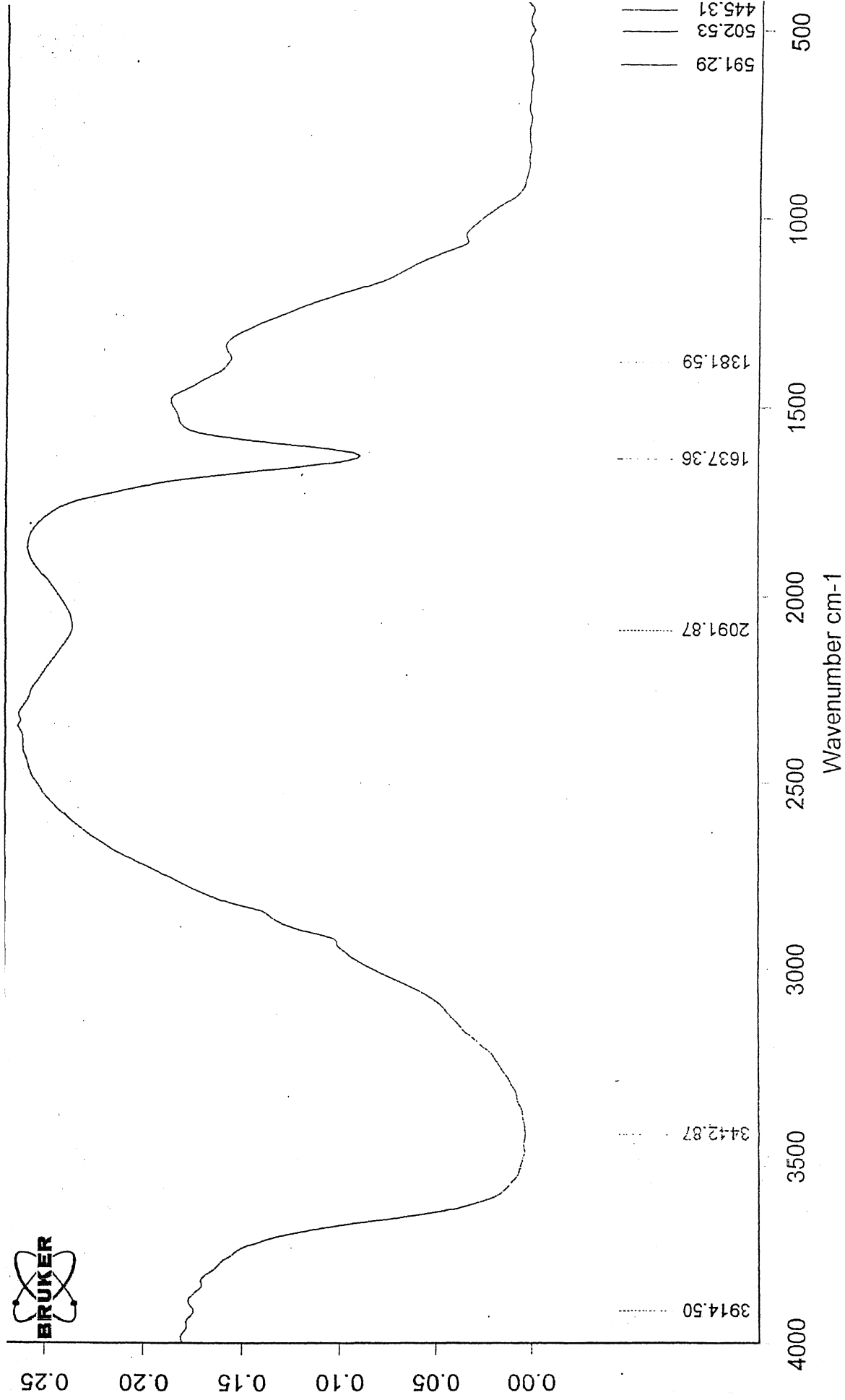


Fig 3.1. FTIR Spectra of dried alumina

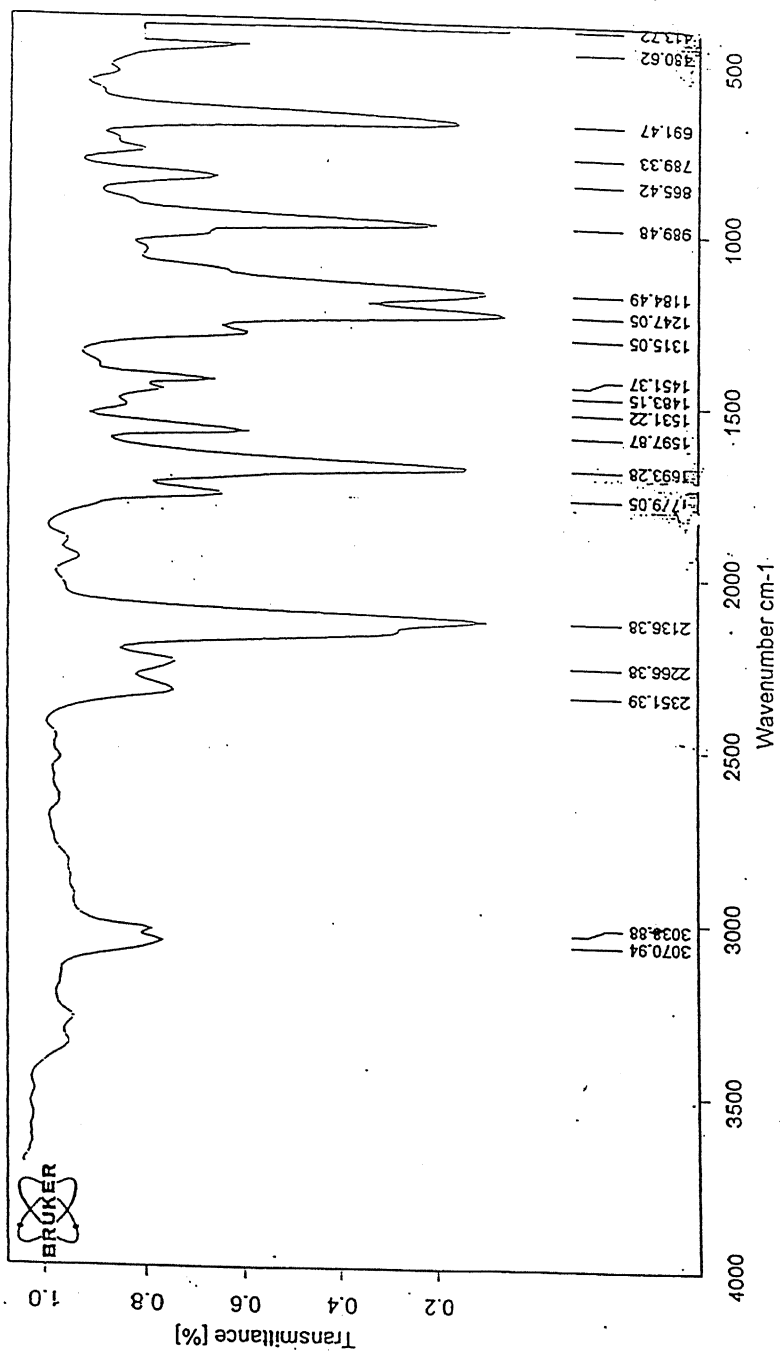


Fig 3.2. FTIR Spectra of phenyl isocyanate

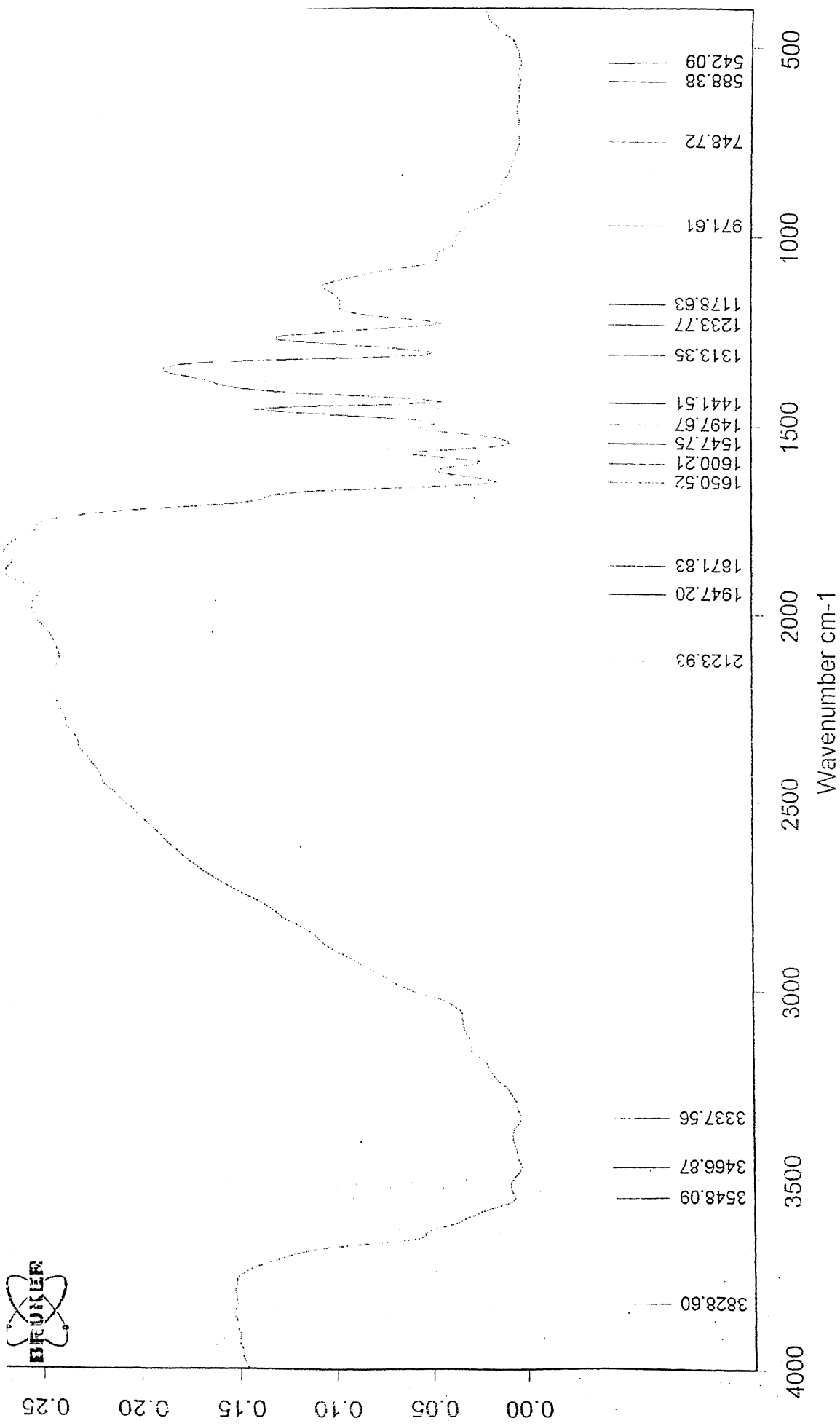


Fig 3.3. FTIR Spectra of carbamated alumina

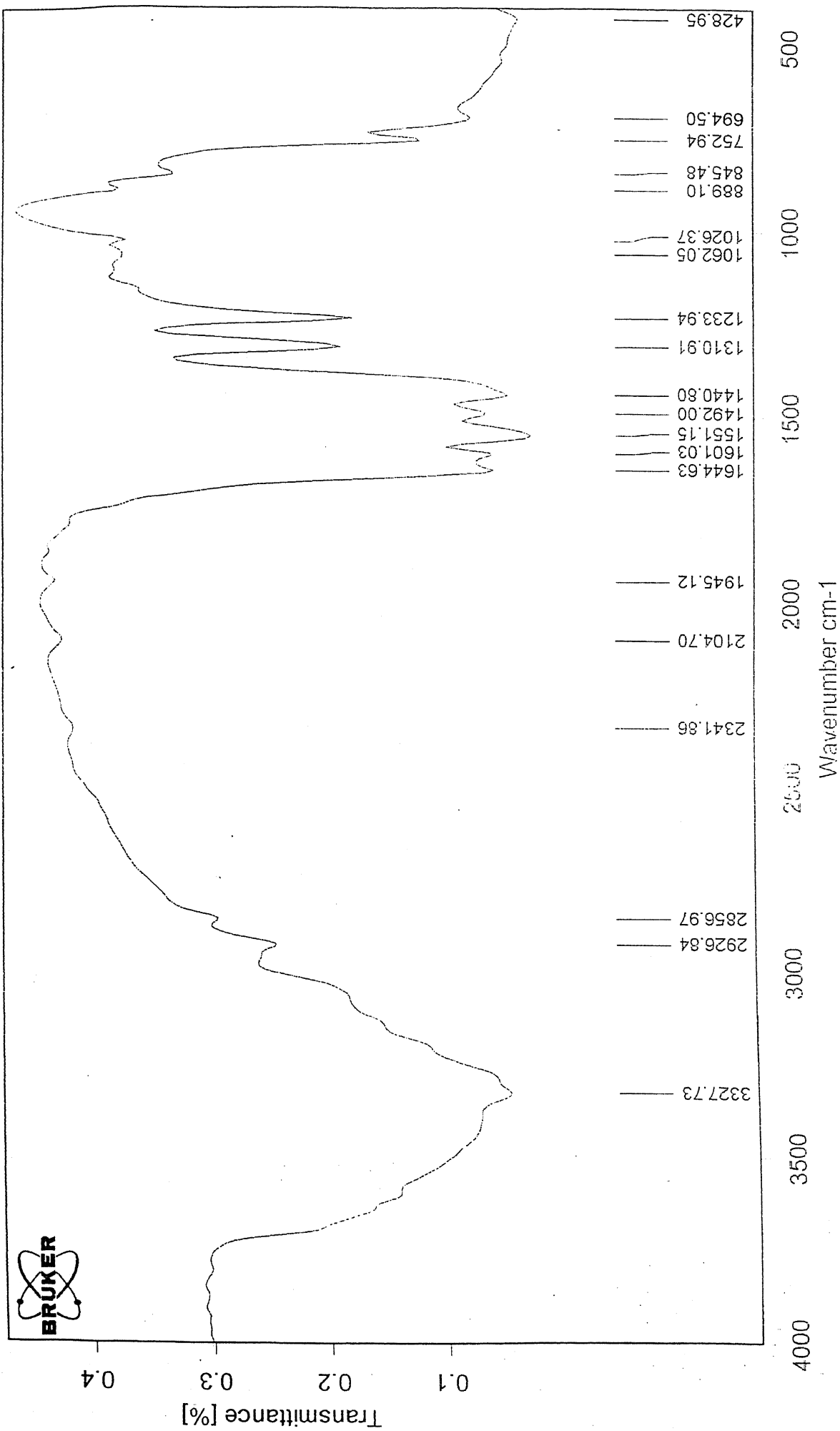


Fig 3.4. FTIR Spectra of carbamated alumina reacted with 1,2-dichloroethane

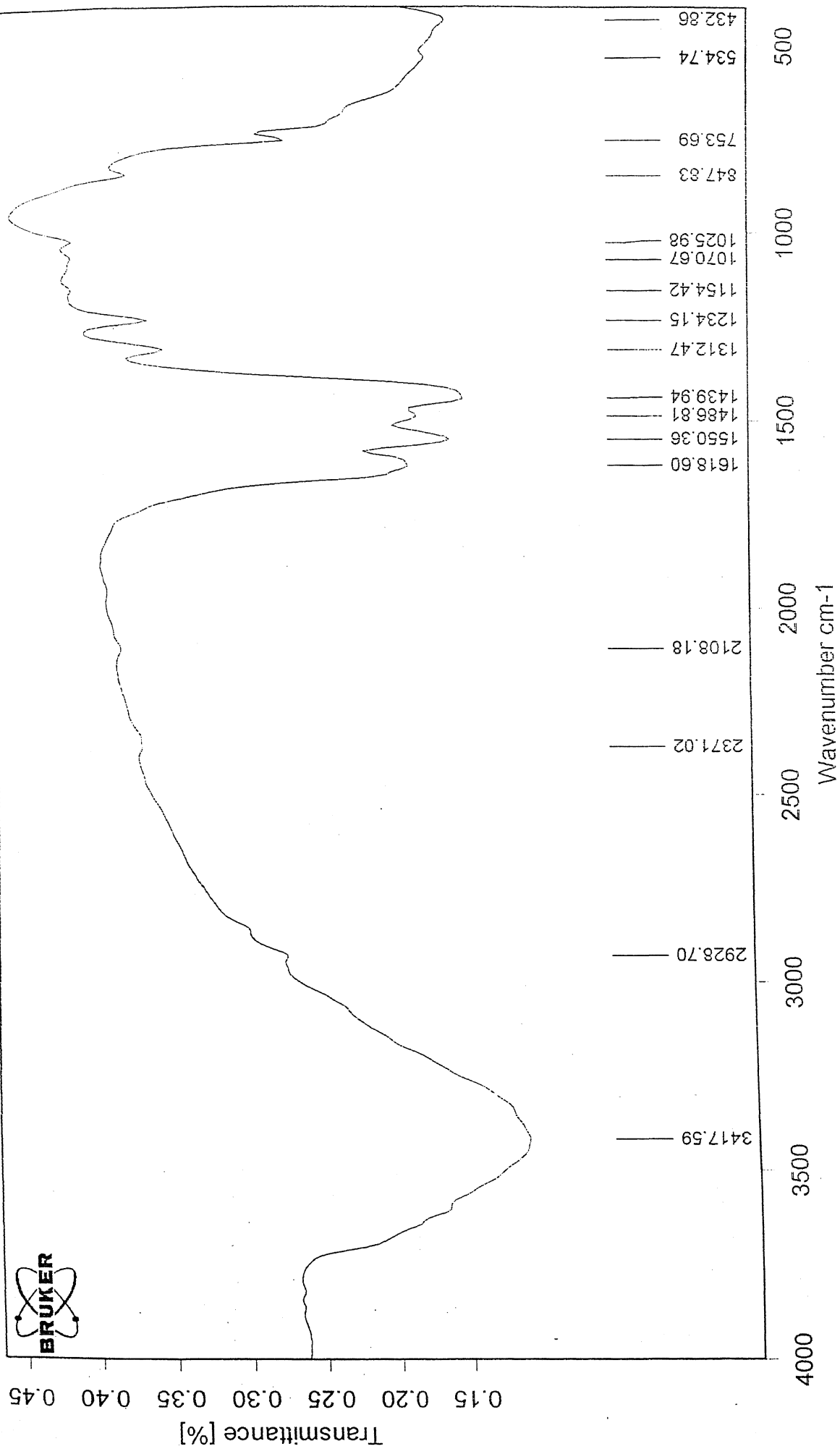


Fig 3.5. FTIR Spectra of final catalyst

3.2 Surface Area Measurement

The surface area is measured on a Coulter SA 2100 instrument, and is analyzed by BET method. The surface area of modified alumina and the mono and bimetallic catalysts (fresh and used) are given in table: 3.1. As seen from the table, there is a fall in surface area of the catalyst after the catalyst is used (after 3 runs). This decrease is more in the case of bimetallic catalysts than in monometallic catalyst.

3.3. Temperature Programming Reduction (TPR)

The TPR technique is used to find the reducing conditions of a substance. In this, the sample a reducing gas (5% H₂ in an inert gas) is flowed over the sample and heated upto 1100°C. A thermal conductivity detector monitors the reaction between the sample and reducing gas and the temperature Vs signal is recorded. The resultant peak gives the characteristic property of the sample. The TPR measurements are made on a micromeritics Pulse ChemiSorb 2705 instrument and the TPR profiles are shown in fig.3.6

3.4 Scanning Electron Microscopy (SEM)

The SEM pictures of monometallic and bimetallic zirconium catalysts are shown in fig3.7. The photographs showed that the chemical reaction produced no change on the surface of the catalyst.

3.5. Powder X-ray Diffraction(XRD)

The XRD patterns of pure alumina, bimetallic zirconium-zirconium catalyst is shown in fig 3.8. The peaks of the metal and alumina are identified and marked.

Table 3.1: The BET surface areas of fresh and used catalysts

Catalyst	Fresh (m ² /g)	Used (m ² /g)
Al ₂ O ₃	226.45	—
Zr/Al ₂ O ₃	193.36	146.78
Zr-Zr/Al ₂ O ₃	138.91	75.175
Co-Zr/Al ₂ O ₃	169.45	87.24
Co-V/Al ₂ O ₃	144.57	92.81

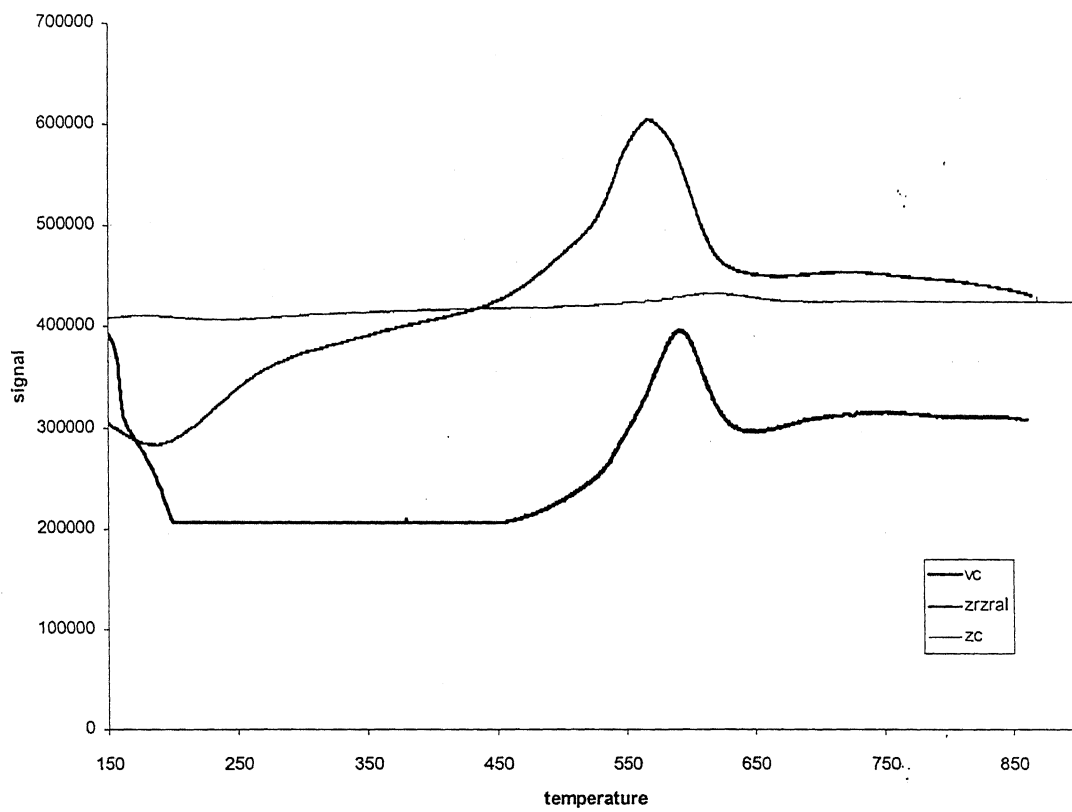


Fig 3.6. TPR profiles of the catalysts

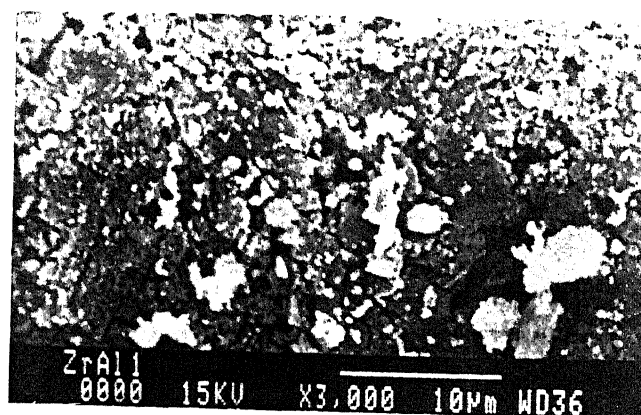
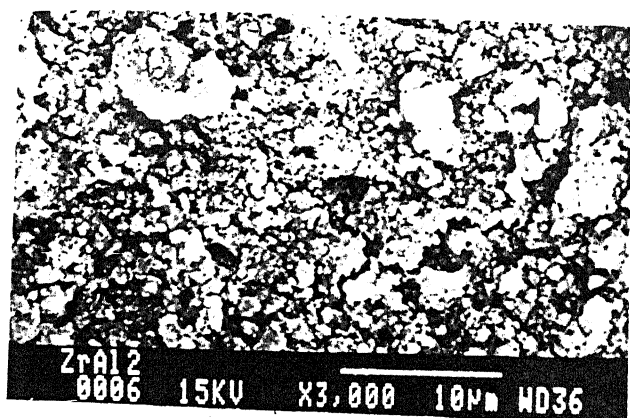
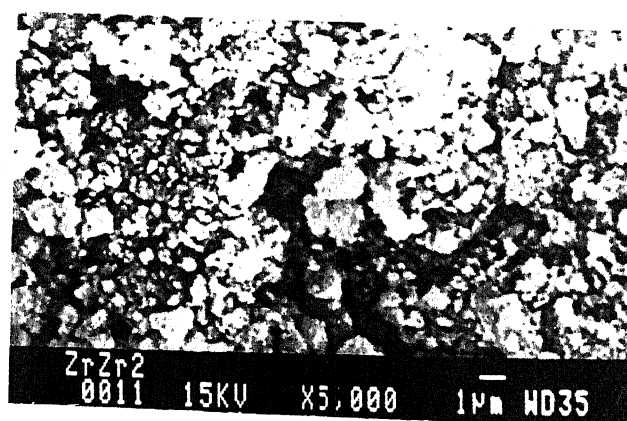
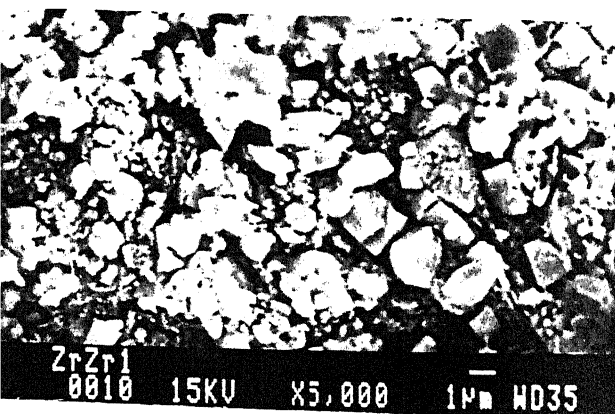


Fig 3.7. a) SEM photographs of monometallic zirconium catalyst



b) SEM photographs of bimetallic zirconium-zirconium catalyst

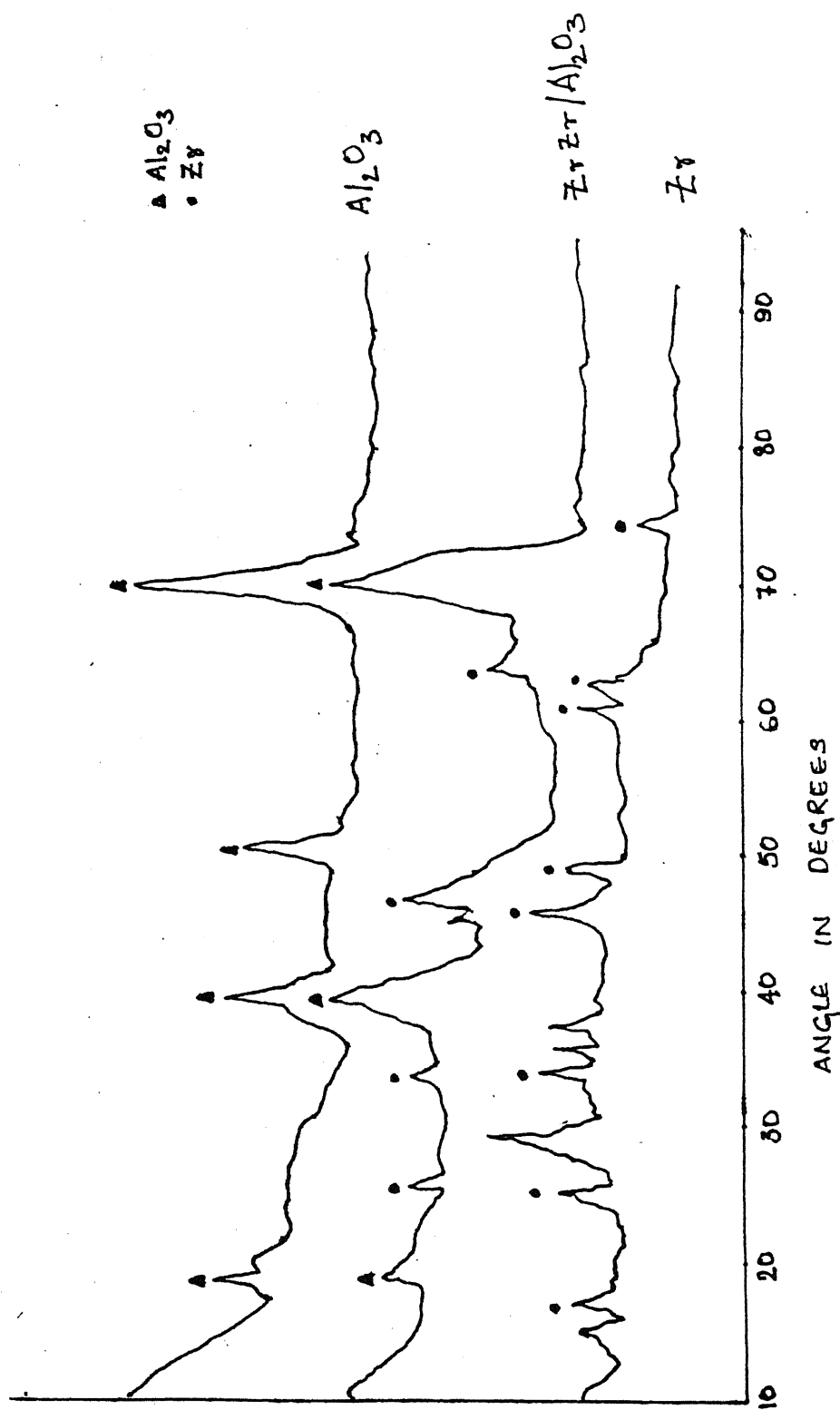


Fig 3.8. XRD pattern of bimetallic zirconium-zirconium catalyst

3.6. Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis is conducted to determine the thermal stability of the catalyst. TGA measures the weight change in a material as a function of temperature (or time). About 10-15 mg of the sample is taken and the weight loss is measured as a function of temperature from 50° C to 980° C. The monometallic catalyst showed stability up to 209°C where as the bimetallic catalyst is stable up to 250°C.

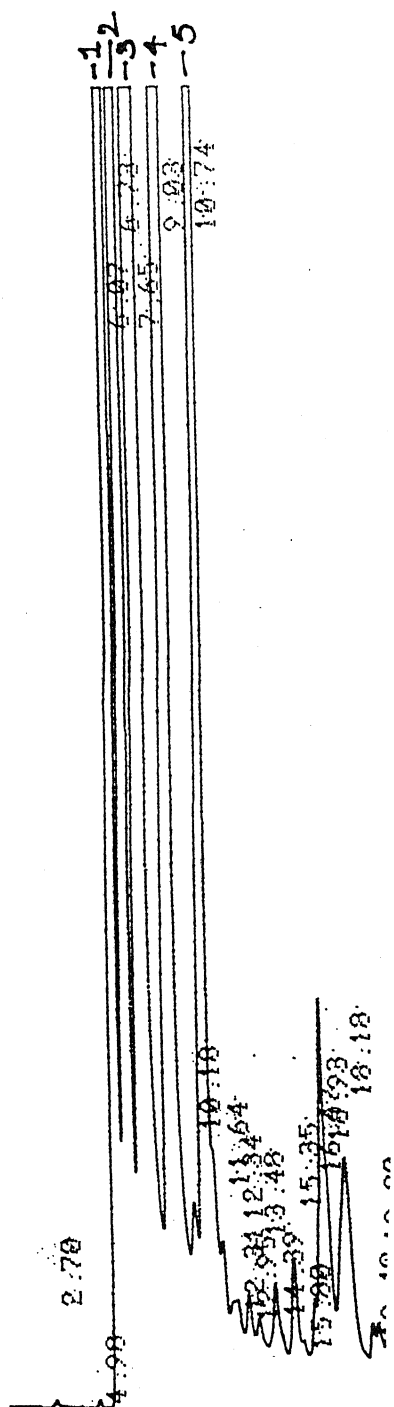
Chapter 4

RESULTS AND DISCUSSION

Isomerization of n-hexane is studied in a batch reactor with catalysts prepared by covalently binding alumina with mono and bimetallic zirconium complexes ($\text{Zr}/\text{Al}_2\text{O}_3$, $\text{Zr-Zr}/\text{Al}_2\text{O}_3$, $\text{Co-Zr}/\text{Al}_2\text{O}_3$). In this study we have systematically varied the reaction times (from 1-6 hours) and temperatures ($150\text{--}200^\circ\text{C}$) in nitrogen and oxygen environments. The analysis of the products is made by Gas Chromatograph Mass Spectroscopy (GCMS). The GCMS data are obtained on a Shimadzu QP-2000 instrument at 70 eV and 250°C and the column used is ULBON HR-1 with fused silica capillary. The products were identified by comparing the mass spectra of the compounds corresponding to the peaks in the gas chromatogram (GC) to that available in the literature. The GC of the product of a run for 2 hours at 200°C with $\text{Zr}/\text{Al}_2\text{O}_3$ in presence of nitrogen at a reaction pressure of 32 atm is shown in fig 4.1. The products are identified as 2-methylpentane (2MP) as peak 1, 3-methylpentane (3MP) as peak 2, Methylcyclopentane (MCP) as peak 4 and cyclohexane as peak 5. The unreacted hexane was identified as peak 3. It can be inferred from that the isomers are mainly formed by dealkylation (2MP and 3MP) and dehydrocyclization (MCP and CH).

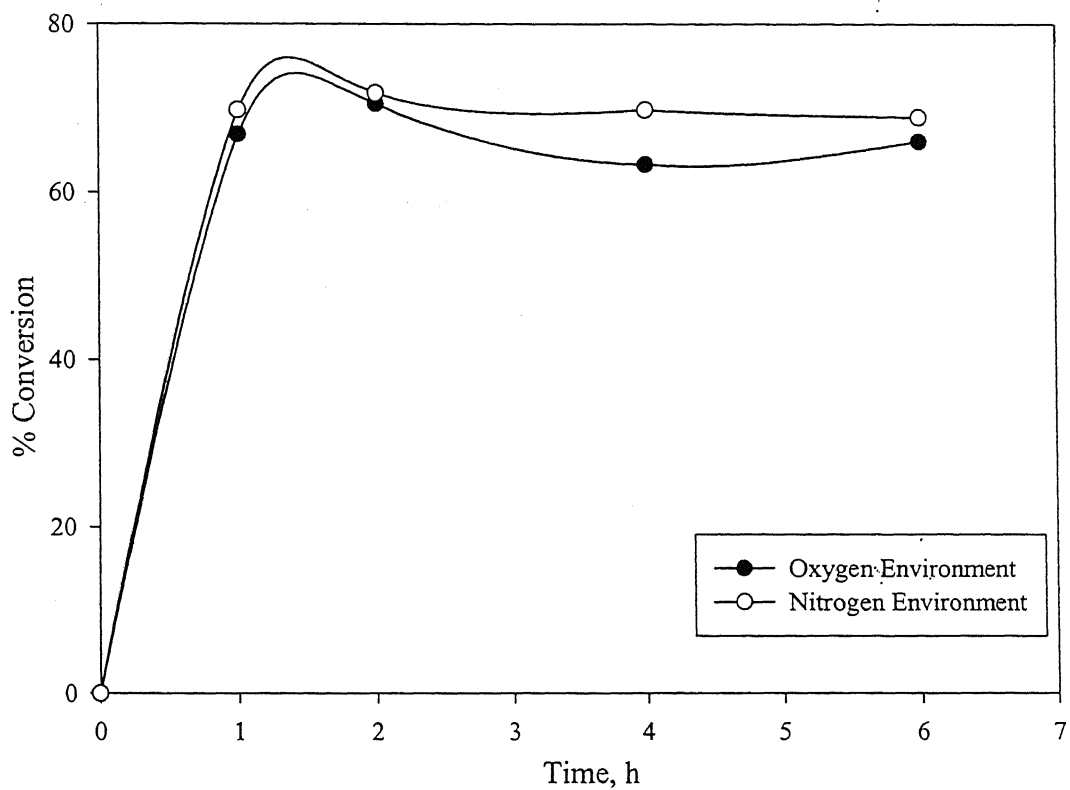
4.1 Effect of Environment on Isomerization of n-hexane

The conversion of n-hexane as a function of reaction time for the runs carried out in presence of oxygen and nitrogen is shown in fig 4.2. The catalyst used is $\text{Zr}/\text{Alumina}$ and the overall conversion of n-hexane is high in case of nitrogen environment (69.9%) than that in oxygen (66.2%). The selectivity of 2MP, 3MP and MCP is the same in the initial time, but is higher for nitrogen as reaction time is increased. For CH, the selectivity is high in oxygen atmosphere than in nitrogen. The total selectivity of products is 96.76% in nitrogen environment and 93.4% in oxygen. The yield of products is shown in fig 4.4. The yield of MCP is highest of all products and that of CH is lowest.

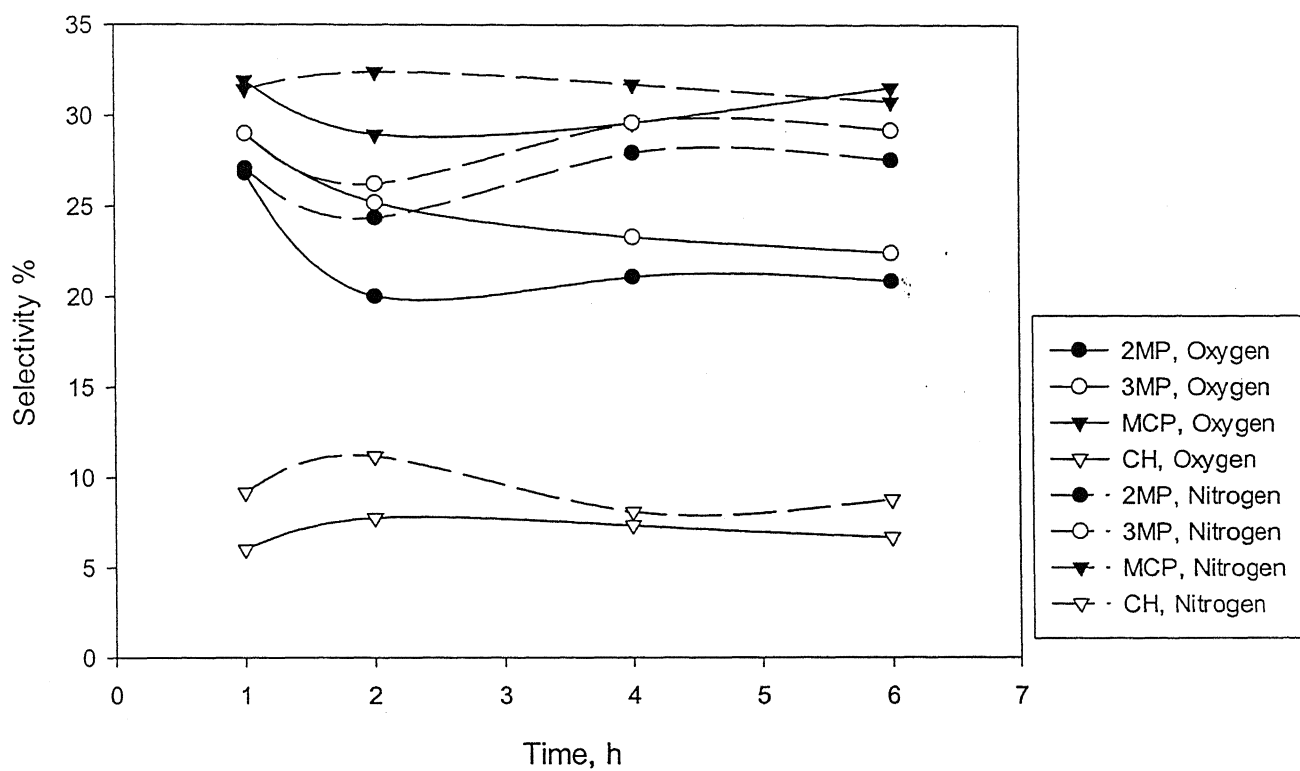


- Peak 1: 2-Methylpentane
- Peak 2: 3-Methylpentane
- Peak 3: n-Hexane
- Peak 4: Methylcyclopentane
- Peak 5: Cyclohexane

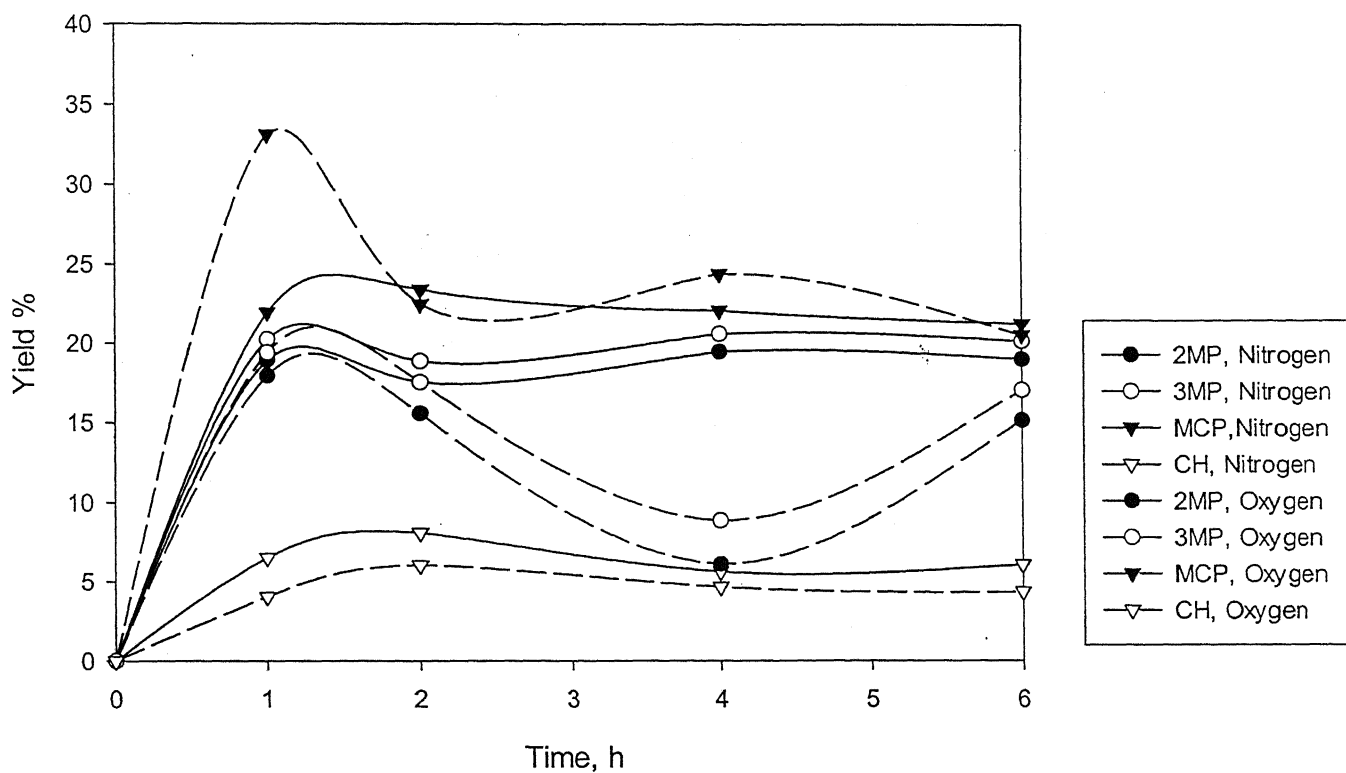
Fig 4.1. Gas chromatograph of products formed on isomerization of n-hexane



4.2 Effect of environment on the conversion of n-hexane isomerization



4.3 Effect of environment on the selectivity of products on n-hexane isomerization



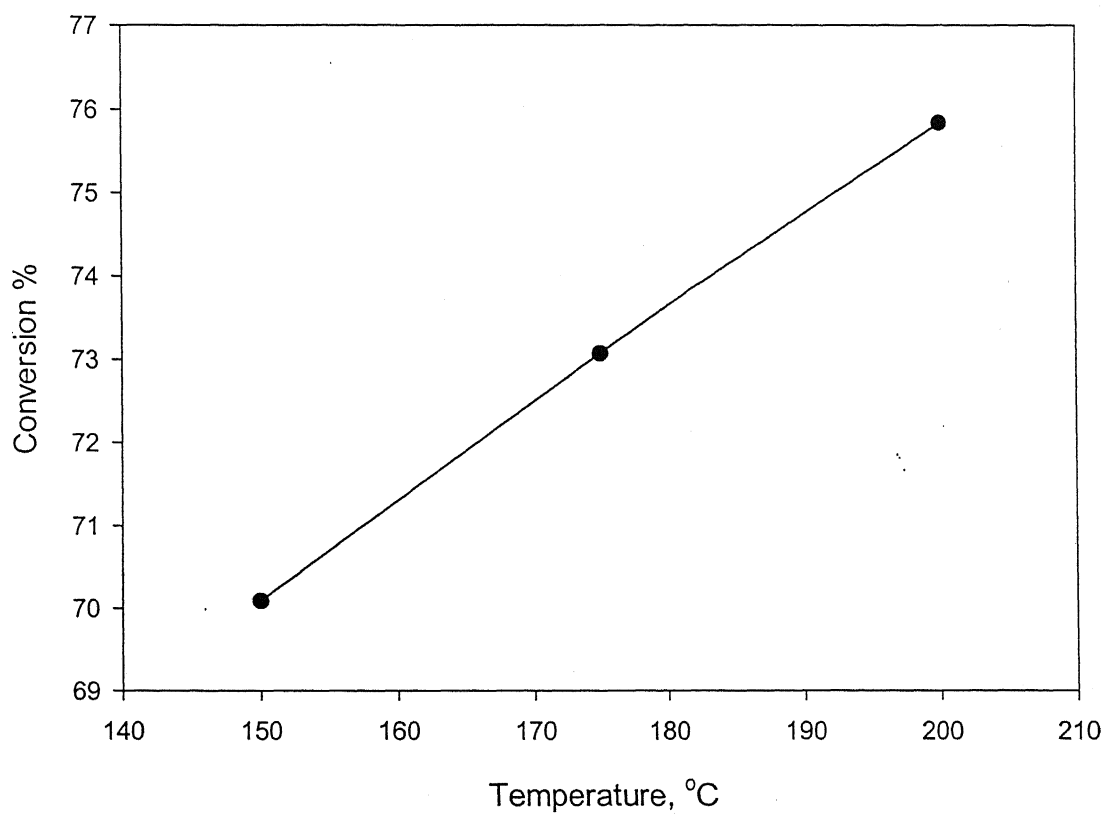
4.4 Effect of environment on the yield of compounds on n-hexane isomerization

4.2. Effect of temperature on total conversion, selectivity and yield

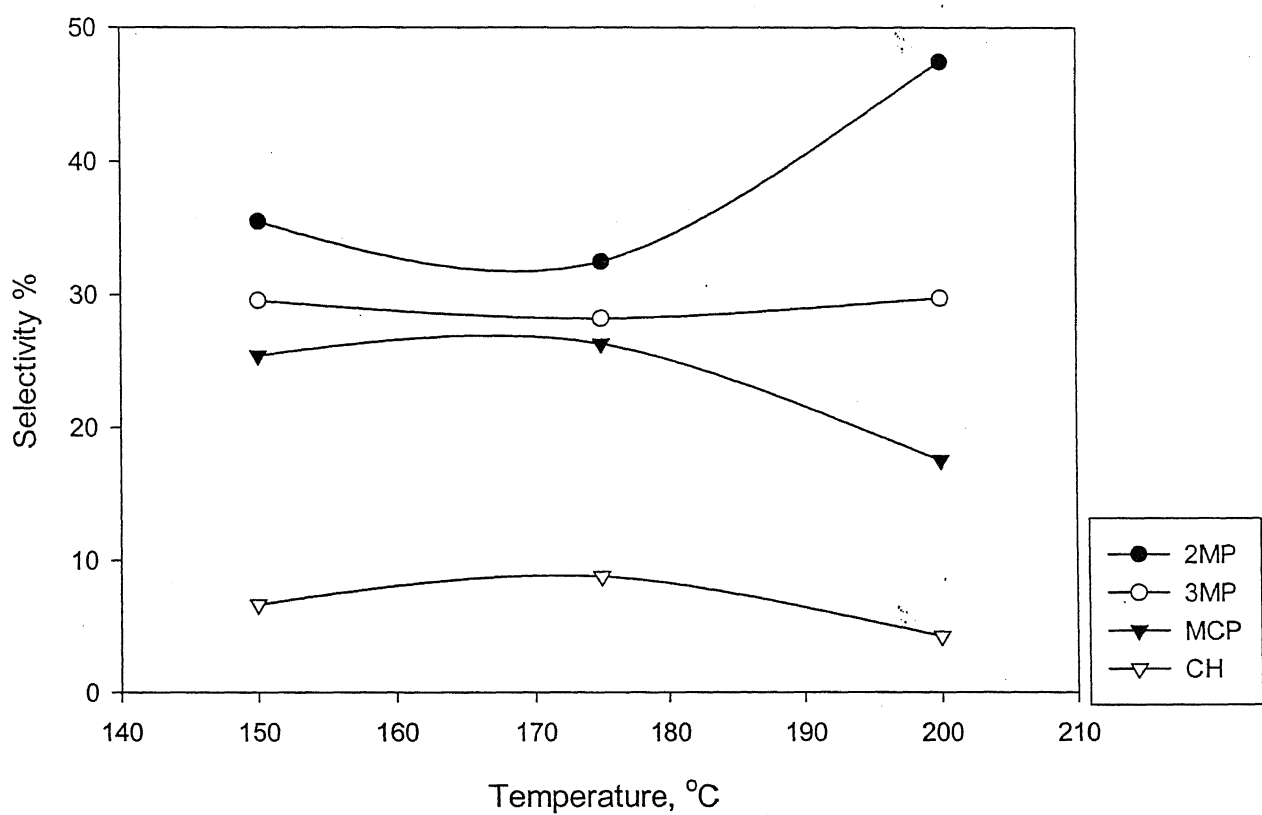
The effect of temperature was studied for n-hexane isomerization with bimetallic zirconium-zirconium (Zr-Zr/Alumina) catalyst in the temperature range 150 - 200°C in nitrogen atmosphere. The overall conversion increased with time as shown in fig 4.5. The selectivity and yield of products is shown in fig 4.6 and fig 4.7. The selectivity of 3MP is constant with temperature and that of MCP and CH is decreased. In the case of 2MP, the selectivity increased with temperature. The yield of 3MP, MCP and CH decreased with temperature whereas for 2MP, it has decreased.

4.3. Effect of catalyst on total conversion, selectivity and yield

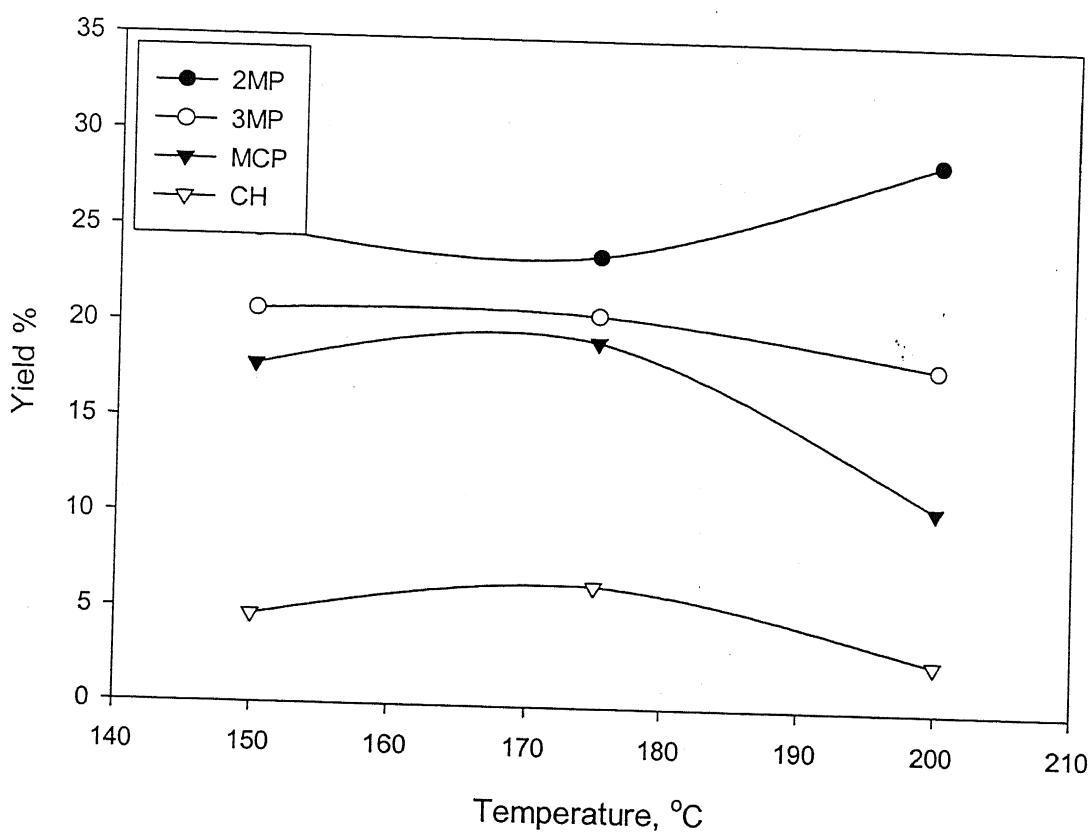
The effect of catalyst on total conversion is shown in fig 4.8 for monometallic zirconium (Zr/Alumina), bimetallic zirconum-zirconium (Zr-Zr/Alumina), and cobalt-zirconium (Co-Zr/Alumina). The overall conversion is high for Co-Zr/Alumina and low for Zr-Zr/Alumina. The selectivity and yield of the products for Zr/Alumina and Zr-Zr/Alumina is shown in fig 4.9 and 4.10 respectively. The selectivity of MCP and 3MP is high for Zr-Zr/Alumina whereas for 2MP and CH it is low. The yield of CH and MCP is high for Zr/Alumina and low for 2MP and 3MP.



4.5 Effect of temperature on conversion of n-hexane isomerization



4.6 Effect of temperature on selectivity of products formed on n-hexane isomerization



4.7 Effect of temperature on yield of products formed on n-hexane isomerization

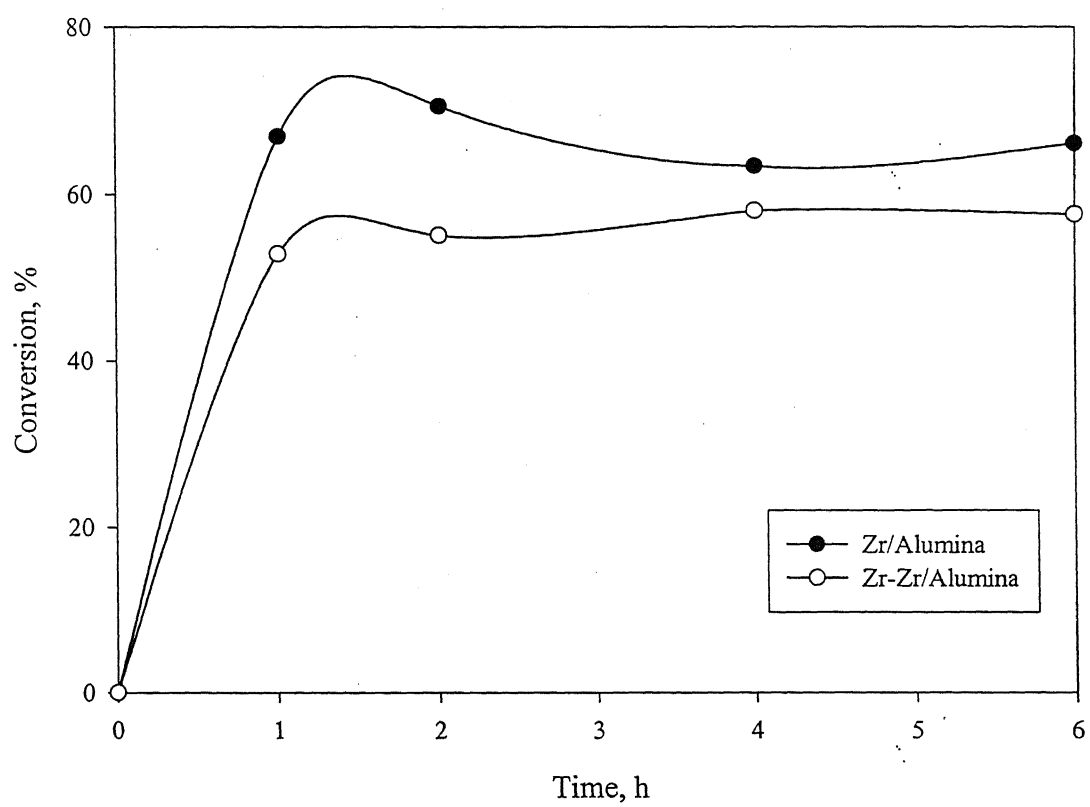
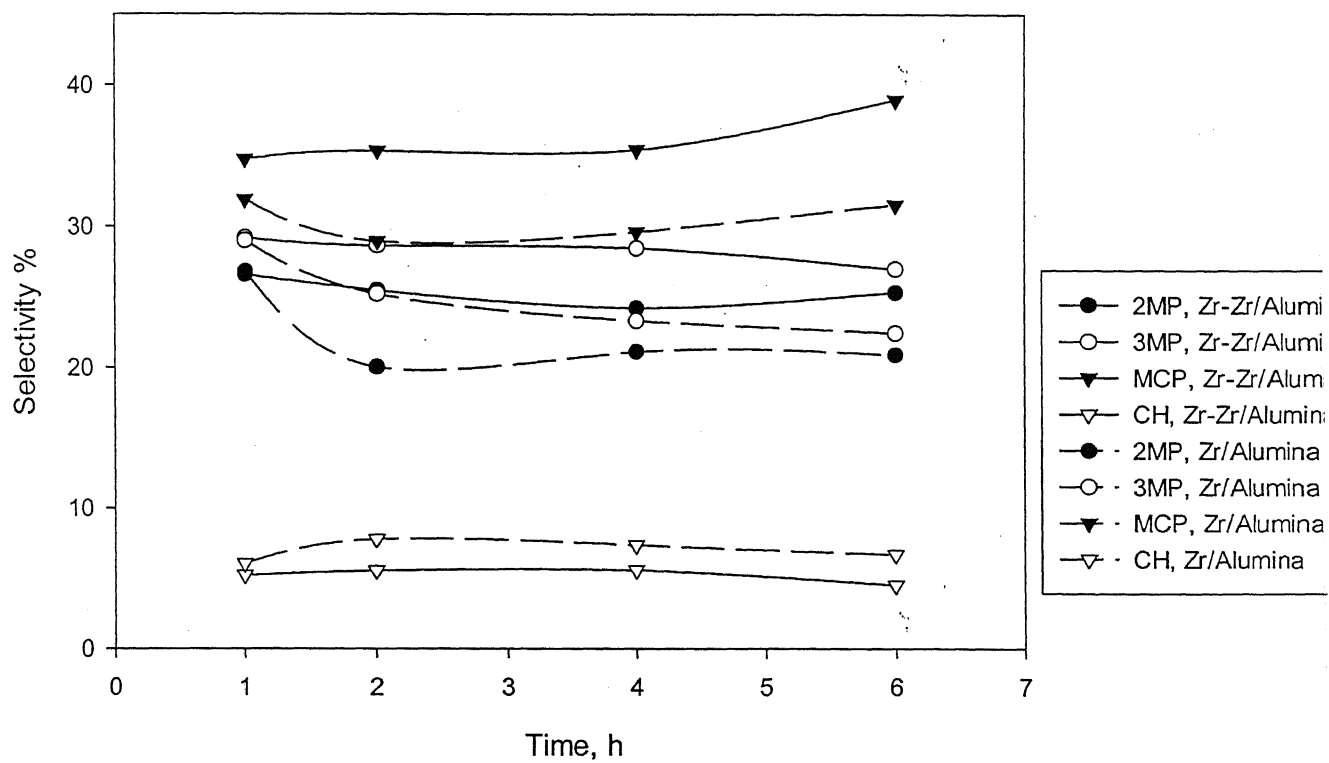
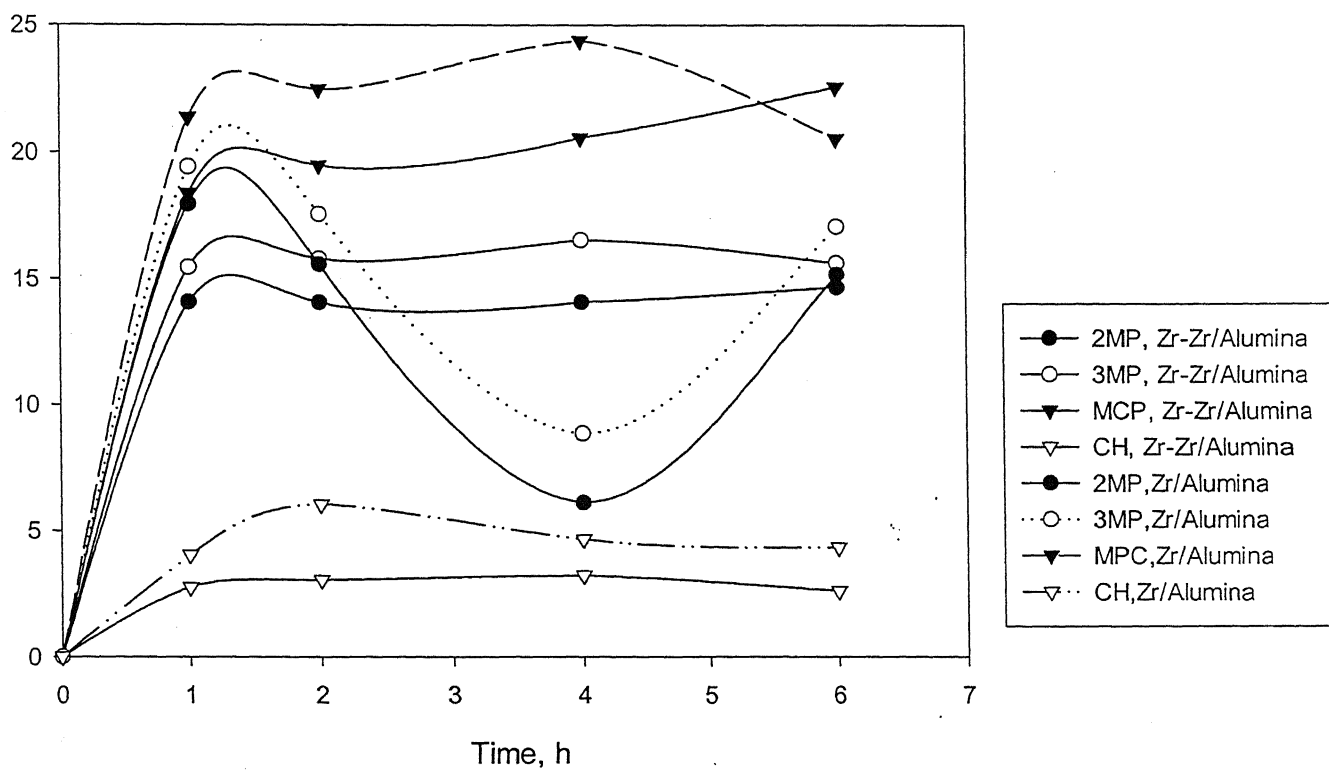


Fig:4.8 Effect of catalyst on conversion of n-hexane isomerization



4.9 Effect of catalyst on the selectivity of products formed on n-hexane isomerization



4.10 Effect of catalyst on the yield of products formed on n-hexane isomerization

Chapter 5

CONCLUSIONS

We synthesized 2,6-diformyl-4-methylphenol using the procedure given in the literature and prepared the bimetallic complex. This complex was covalently bound to phenyl isocyanate modified alumina. The experimental results with this catalyst were found to be the following

1. The compound synthesized was identified as 2,6-diformyl-4-methylphenol by matching the NMR spectra and the melting point results with those given in the literature.
2. The bimetallic complexes were analyzed by the FTIR and the CHN analysis. The former matched with that of literature, but the later has discrepancies in the C-values.
3. The bimetallic catalyst was subjected to the XRD analysis and it confirmed both metals on the surface of the alumina.
4. The SEM analysis showed that the catalyst surface was unaffected by the isomerization reaction carried upto 200°C.
5. The TGA analysis showed that the bimetallic catalyst was more stable compared to the monometallic complex formed by complexing zirconium with 1,2 bis-(salicylidene amino)-phenylene.
6. The monometallic catalyst was more active giving higher conversion for isomerization of hexane compared to bimetallic catalysts. The products formed for each of these catalysts have been 2MP, 3MP, MCP, CH with CH being the lowest.
7. Oxygen environment is found to lower the final conversion reached for isomerization reactions compared to nitrogen.
8. The total conversion for both these catalysts increased with the increase in temperature.
9. The selectivity of MCP and CH decreased with temperature, while that of 2MP and 3MP increased.
10. The yield of 2MP increased with temperature while that of 3MP, MCP and CH decreased with temperature.

References

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Appendix1

Calculation of C-H-N Values:

$$\text{C Value: } \frac{N_C \times 12}{M_C}$$

$$\text{H Value: } \frac{N_H \times 1}{M_C}$$

$$\text{N Value: } \frac{N_N \times 14}{M_C}$$

$$M_C = N_C \times 12 + N_H \times 1 + N_N \times 14 + M_A + M_B$$

Where

N_C : Number of carbons present in the molecule

N_H : Number of hydrogens present in the molecule

N_N : Number of nitrogens present in the molecule

M_A : Molecular weight of metal A

M_B : Molecular weight of metal B

1. Calculation of conversion:

The overall percentage conversion of reactant is calculated as

$$\% \text{ conversion} = \left(1 - \frac{\text{number of moles of reactant in}}{\text{number of moles of reactant out}} \right) * 100$$

2. Calculation of selectivity:

The selectivity of a particular product is given as

$$\% \text{ selectivity} = \left(\frac{\text{number of moles of product out}}{\text{number of moles of reactant consumed}} \right) * 100$$

3. Calculation of yield:

The yield of a particular product is given as

$$\% \text{ yield} = \left(\frac{\text{number of moles of product out}}{\text{number of moles of reactant in}} \right) * 100$$

Appendix2

Mass Spectra of compounds obtained by Mass Spectroscopy analysis of the products and matched with literature

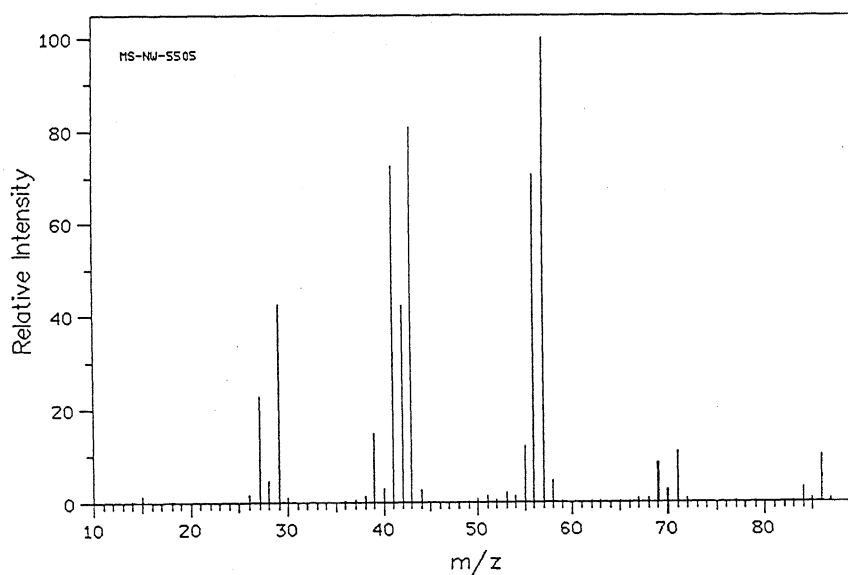


Fig A2.1 Mass Spectra of n-Hexane

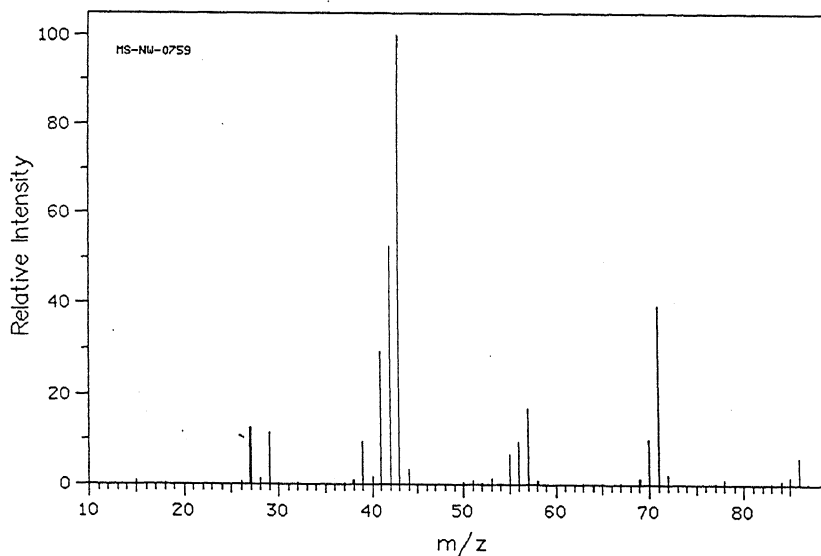


Fig A2.2 Mass Spectra of 2-Methylpentane

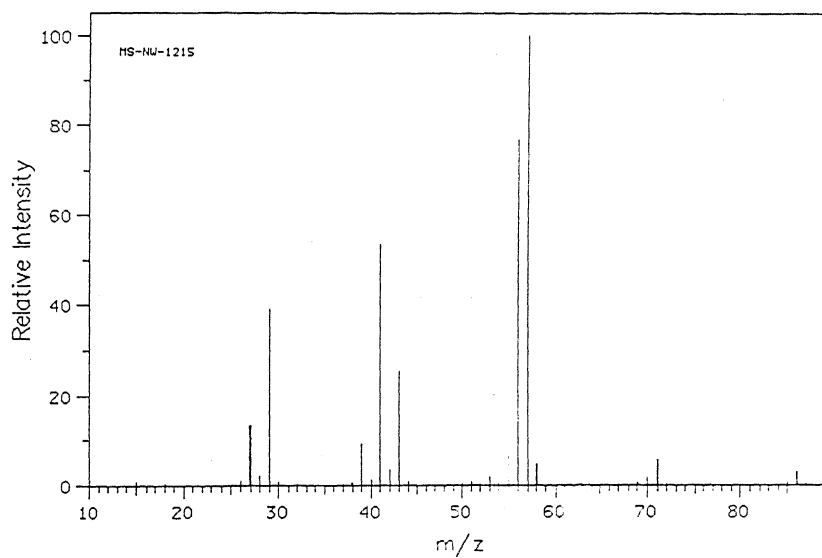


Fig A2.3 Mass Spectra of 3-Methylpentane

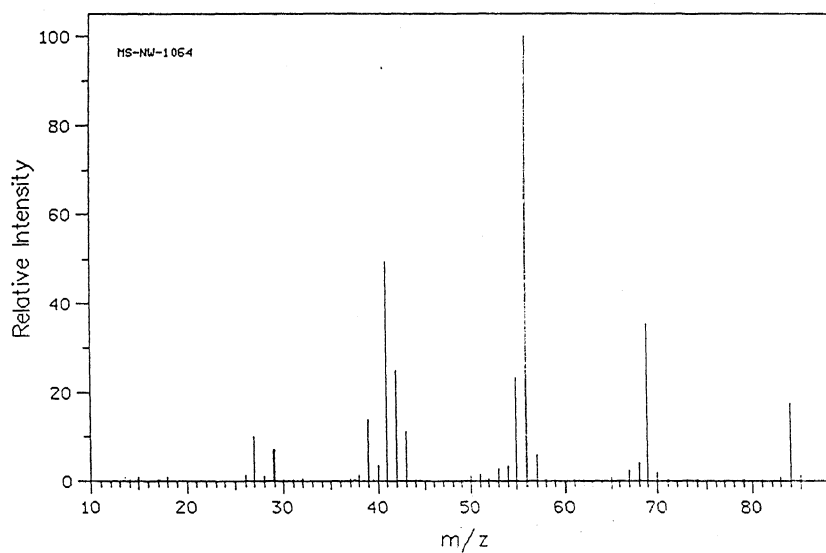


Fig A2.4 Mass Spectra of Methylcyclopentane

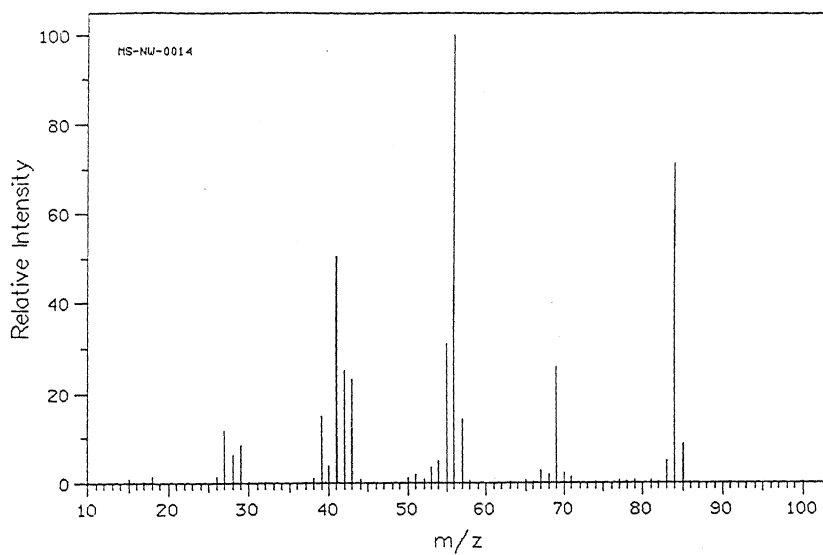


Fig A2.5 Mass Spectra of Cyclohexane

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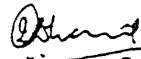
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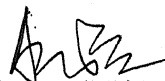
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All interested are cordially invited.

Time: 10:00 AM

Date: 2nd January 2002.

Venue: NL- II, 205



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